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A

DICTIONARY OF CHEMISTRY.

SUPPLEMENT.

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A DICTIONARY

OF

CHEMISTRY

AND THE

ALLIED BRANCHES OF OTHER SCIENCES.

BY

HENRY WATTS, B.A., F.R.S., F.C.S.

EDITOR OF
'THE JOURNAL OF THE CHEMICAL SOCIETY.'

ASSISTED BY EMINENT CONTRIBUTORS.

SUPPLEMENT.

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PREFACE.

THE present Supplement brings the Record of Chemical Discovery down to the end of the year 1869, including also several additions to, and corrections of, former results which have appeared in 1870 and 1871.

The author has been fortunate in obtaining the assistance of some of the former Contributors to the Dictionary, to whom he begs to tender his best thanks. The following is a list of their names and contributions:—

G. C. Foster, B.A., F.R.S. . . .	Electricity.—Heat.
Michael Foster, M.D. . . .	Proteids.
Benjamin H. Paul, Ph.D. . . .	Beer.—Iron, Metallurgy of.
H. E. Roscoe, Ph.D., F.R.S. . . .	Light, Chemical Action of.—Spectral Analysis.
J. A. Wanklyn, *Corresponding Member of the Royal Bavarian Academy of Sciences*	Acetic Ether (in part).—Butyl Alcohols.—Butyric acid (in part).—Ethyl, Acetylinated.—Ketones.

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DICTIONARY OF CHEMISTRY.

SUPPLEMENT.

A

ABIES. The needles of *Abies pectinata* contain a sugar called abietite, very much like mannite, but differing therefrom by its relations to solvents, and by its composition, which is represented by the formula $C^6H^8O^3$: it contains, therefore, $3H^2O$ less than mannite, $2H^2O$ less than quercite, and H^2 more than phloroglucin.

To separate the proximate principles contained in the needles, they were first exhausted with boiling alcohol, then with water; the aqueous decoction was precipitated by neutral lead acetate, and the precipitate, after washing with water, was treated with acetic acid, in which it is only partially soluble. The soluble portion was neutralised with ammonia, and re-precipitated by basic lead acetate; and this last precipitate, decomposed by hydrogen sulphide, yielded a tannin identical with the soluble tannin of the horse-chestnut, $C^{13}H^{12}O^6$. This tannin is transformed into an insoluble modification by adding hydrochloric acid to its solution, then agitating the liquid with six or eight volumes of ether, and leaving the whole to itself for ten or twelve hours. The precipitate thus obtained forms, after washing and drying, a chamois-coloured powder, insoluble in water, ether, and acetic acid, slightly soluble in boiling alcohol and in potash, which latter colours it red-brown. This insoluble tannin dissolves, however, in boiling potash, and when it is boiled with water and alcohol, a small quantity dissolves, forming a red liquid. The conversion of the soluble into the insoluble tannin is attended with loss of water; the latter has the composition $C^{52}H^{46}O^{23}$. (Rochleder, J. pr. Chem. cv. 63, 123.)

The fruits of *Abies Reginæ Amaliæ*, indigenous in Arcadia, yield, by distillation with water, about 18 per cent. of a colourless volatile oil, $C^{10}H^{16}$, having a fragrant odour of lemons, a specific gravity of 0·868, boiling at 156–159°, slightly lævo-gyrate. It resinises quickly in the air, exerting at the same time a stronger ozonising action than common turpentine oil. It dissolves iodine without rise of temperature, and absorbs hydrochloric acid gas, forming a liquid compound, $C^{10}H^{16}.HCl$. (Buchner a. Thiel, J. pr. Chem. xcii. 109.)

ABIETIC ACID. See Sylvic Acid.

ABIETITE. See Abies.

ABSINTHIN or **ABSYNTHIIN.** This substance, the bitter principle of wormwood (*Artemisia Absynthium*), has been re-investigated by A. Kromayer (Arch. Pharm. [2] cviii. 129; Jahresb. 1861, p. 745). The mode of preparation adopted consists mainly in exhausting the dry herb of the plant with hot water; treating the concentrated extract with animal charcoal, which absorbs the bitter principle; then extracting it with alcohol, partially purifying it by treatment with lead-acetate, &c., as described at p. 2, vol. i.; then dissolving it in alcohol, precipitating it with tannic acid; washing the precipitate with water and weak spirit; dissolving it in strong alcohol; mixing it with levigated lead-oxide; evaporating the mixture after addition of a little water; boiling out the dry residue with alcohol; and leaving the colourless filtered liquid to evaporate slowly in a moderately warm place. Absinthin then remains as a yellowish pulverulent mass, neutral, having an intensely bitter taste, and an aromatic odour like that of wormwood, nearly insoluble in cold, somewhat more soluble in hot water, easily in alcohol and ether. From the alcoholic solution it is gradually precipitated by water in white flocks. It melts between 120° and 125°, and decomposes at a stronger heat, giving off pungent vapours. Strong sulphuric acid dissolves it with brownish, afterwards greenish-blue colour, changing, on addition of a few drops of water, to a splendid blue, which disappears on further addition of water. When an alcoholic solution of absinthin is mixed with an equal volume of strong sulphuric acid, a brown-red mixture is formed which, on addition of a few drops of water, assumes a beautiful violet colour. Absinthin boiled with dilute sulphuric acid is converted into a brown resin, and the supernatant red-brown solution exhibits a beautiful yellow-green iridescence by reflected light. This solution does not contain sugar; neither is sugar produced by treating absinthin with strong hydrochloric acid. Strong nitric acid attacks absinthin only when heated; on mixing an alcoholic solution of absinthin with water till it begins to show turbidity, and then with solution of tannic acid, a pure white precipitate of tannate of absinthin is obtained, which assumes the consistence of a plaster when stirred, and after washing and drying at 100°, forms a greyish, easily pulverised mass. Absinthin does not reduce an alkaline solution of cupric oxide, but when warmed with ammoniacal silver nitrate forms a speculum of metallic silver. Solutions of absinthin are not precipitated by metallic salts.

The analysis of pure absinthin yielded numbers answering to the formula $C^{40}H^{58}O^9$, or $2C^{20}H^{28}O^4.H^2O$. Kromayer regards it as an aldehyde.

ACANTHITE. A rhombic or trimetric variety of silver sulphide Ag^2S (v. 304), occurring at Freiberg and Joachimsthal (Kenngott, Pogg. Ann. xcv. 462; Dauber, Jahresb. 1860, p. 747). According to Breithaupt (*ibid.* 1863, p. 796), it mostly occurs in twins very much like those of diopside.

ACAROÏD RESIN. This resin yields, by oxidation with melting potash, so large a quantity of paraoxybenzoic acid (36 grms. from 9 ounces) that it may be conveniently used as a source of that acid. The mother-liquor of the ethereal extract contains also resorcin and pyrocatechin, as well as the double compound of protocatechuic and paraoxybenzoic acids, $C^{14}H^{12}O^7.H^2O$, first obtained from benzoin (Hlasiwetz a. Barth. Jahresb. 1866, p. 630).

ACECONITIC ACID. $C^6H^6O^6 = \left.\begin{matrix}(C^6H^3O^3)'''\\ H^3\end{matrix}\right\}O^3 = (C^3H^3)'''(COHO)^3$.* (A. Baeyer, Berl. Akad. Ber. 1864, p. 584; more fully, Ann. Ch. Pharm. cxxxv. 306; Jahresb. 1864, p. 397; 1865, p. 394.)

A tribasic acid produced, together with citracetic acid—an acid of nearly the same composition, and likewise tribasic—by heating ethylic bromacetate with sodium. The product of the reaction is a smeary brown mass, which by evaporation in a vacuum yields a non-separable mixture of the ethers of the two acids just mentioned, boiling above 200°. The solution of this crude ether in baryta-water yields, by evaporation, sparingly soluble barium aceconitate and easily soluble barium citracetate. The aceconitate was deposited in crystals, which, however, did not yield definite results on analysis, but the silver-salt prepared by decomposing them with sulphuric acid, neutralising with ammonia, and precipitating with silver nitrate, gave numbers agreeing with the formula $C^6H^3Ag^3O^6 + 2$ aq.; showing that aceconitic acid is represented by the formula $C^6H^6O^6$, and is isomeric with aconitic acid. The formation of the ether probably takes place by two stages, the sodium first taking the place of an atom of hydrogen in the acetyl molecule of the bromacetic acid, and sodium bromide being afterwards eliminated:

$$(1)\qquad \left.\begin{matrix}C^2H^2BrO\\ C^2H^5\end{matrix}\right\}O + Na = \left.\begin{matrix}C^2HNaBrO\\ C^2H^5\end{matrix}\right\}O + H$$

$$(2)\qquad 3\left.\begin{matrix}C^2HNaBrO\\ C^2H^5\end{matrix}\right\}O = 3NaBr + \left.\begin{matrix}C^6H^3O^3\\ (C^2H^5)^3\end{matrix}\right\}O^3.$$

Free aceconitic acid crystallises in warty groups of needles like aconitic acid, but more easily and in better defined forms than the latter; it is likewise easily soluble in water. When heated it melts and burns, leaving a small quantity of charcoal; when warmed in a test-tube it does not yield any crystalline sublimate. The *barium salt* crystallises in small sparingly soluble crystals; the solution of the *calcium salt* becomes turbid when heated, like that of the citrate; with neutral lead acetate and mercurous nitrate the acid forms white precipitates.

Citracetic acid and its salts are uncrystallisable, and therefore very difficult to purify; they give, however, by analysis numbers agreeing nearly with those of the corresponding aconitates, so that citracetic acid is probably another isomer of aconitic acid.

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* In Baeyer's preliminary notice, aceconitic acid was represented by the formula $C^6H^8O^6$, the same as that of carballylic acid.

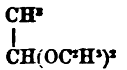
ACENAPHTHENE or **ACETYLONAPHTHALENE.** $C^{12}H^{10} = C^{2}H^{2}.C^{10}H^{6}$ (Berthelot, Bull. Soc. Chim. [2] viii. 226; Jahresb. 1867, p. 594).—A hydrocarbon occurring in the portion of heavy coal-tar oil which distils between 260° and 340°. When the portion distilling between 270° and 290° is separated by fractional distillation and left at rest, acenaphthene separates in large transparent prisms, and a further quantity may be obtained from the mother-liquor by repeated distillation and cooling. It is purified by pressing the crystals between paper, dissolving them in ten to fifteen times their weight of boiling alcohol, and leaving the solution to cool very slowly. Acenaphthene is also contained in the solid hydrocarbons which crystallise gradually from the tar-oils distilling between 300° and 400°, and passes over in the distillation of these oils, together with fluorene. If the solid distillate thus obtained be re-crystallised, the fluorene separates out first, while the acenaphthene accumulates in the mother-liquors, and may be separated therefrom by careful evaporation. It may also be isolated from the solid mixture above mentioned by sublimation in a flask, the bottom of which is heated to 100°. Lastly, it is formed when a mixture of naphthalene vapour and ethylene gas is passed through a heated porcelain tube, and may be separated from the products by re-crystallising the portion which distils between 270° and 300° from alcohol.

Acenaphthene crystallises from alcoholic solution in colourless shining needle-shaped prisms, sometimes a decimetre long, and from solution in heavy tar-oils, in bulky hard brittle crystals. Its odour is like that of naphthalene, but fainter. It is heavier than water, melts at a little above 100°, solidifies at 93°, and boils at 284°–285° (corr.). It dissolves easily in boiling alcohol, and separates almost completely on cooling. From a mixture of the alcoholic solutions of acenaphthene and picric acid, the picrate, $C^{12}H^{10}.C^{6}H^{3}(NO^{2})^{3}O$, crystallises quickly in orange-yellow needles; from a solution of equivalent proportions of the two substances in boiling alcohol, it crystallises in laminæ. Evaporated with Fritzsche's re-agent (nitranthracene), acenaphthene forms red needles, partly curved and branching like a fan. In *sulphuric acid*, either fuming or ordinary, it dissolves with formation of acenaphthene sulphuric acid, which is coloured green by small quantities of nitric acid, and forms easily soluble salts. *Nitric* acid acts violently on acenaphthene. If the hydrocarbon be triturated with the acid in a cooled vessel till the acid is saturated, the solution solidifies, after a while, to a crystalline mass of dinitro-acenaphthene, $C^{12}H^{8}(NO^{2})^{2}$, which is nearly insoluble in alcohol even at the boiling heat, sparingly soluble in ether, but dissolves abundantly in boiling light tar-oils, and crystallises from this solution in brown-yellow pointed needles. The mother-liquor of these crystals leaves, on spontaneous evaporation, brown granules of a compound of mono- and di-nitroacenaphthene, $C^{12}H^{9}(NO^{2}).C^{12}H^{8}(NO^{2})^{2}$. Sodium does not act upon acenaphthene. *Potassium* eliminates hydrogen, and forms the compound $C^{12}H^{9}K$, as a black insoluble mass, decomposed by water, with reproduction of acenaphthene. *Bromine* likewise acts strongly upon acenaphthene. On adding it to an ethereal solution of the hydrocarbon till the liquid acquires a yellow colour, and leaving the solution to evaporate, there remains a thickish oil in which a few laminar crystals form, probably consisting of monobromacenaphthene, $C^{12}H^{9}Br$. A solution of acenaphthene in the most volatile portion of American petroleum, mixed in a cooled vessel with a slight excess of bromine (4 pts. bromine to 1 pt. of the hydrocarbon), yields the hexbromide, $C^{12}H^{10}Br^{6}$, which crystallises out in small grains, while a liquid substitution-product remains in solution; by re-crystallisation from boiling alcohol the hexbromide is obtained in slender white needles. Acenaphthene heated to its boiling point with *iodine*, is decomposed, with evolution of hydriodic acid and formation of a carbonaceous substance; at 100° it appears to be converted by iodine into a polymeric compound. Hydrochloric and hydrobromic acids in aqueous solution do not act upon acenaphthene. Heated to 100° with saturated *hydriodic acid*, it forms a liquid hydride, probably $C^{12}H^{12}$, boiling at about 270°, together with the above-mentioned polymeric modification produced by the separated iodine. With 20 pts. hydriodic acid at 280°, it forms, as chief products, naphthalene-hydride and ethyl-hydride:

$$C^{12}H^{10} + 3H^{2} = C^{10}H^{10} + C^{2}H^{6};$$

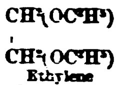
and in smaller quantities, acenaphthene-hydride. With 80 pts. hydriodic acid at the same temperature, it yields decyl-hydride, $C^{10}H^{22}$ (boiling at 160°), as principal products; further octyl-hydride, $C^{8}H^{18}$ (boiling between 115° and 120°), ethyl-hydride, traces of hexyl-hydride, and a substance not volatile at 360°, probably a polymer.

ACETAL. $C^{6}H^{14}O^{2}$.—This compound contains the elements of 1 molecule of aldehyde and 1 molecule ethyl-oxide, $C^{2}H^{4}O.(C^{2}H^{5})^{2}O$; moreover, its several modes of formation from aldehyde, and its re-actions with hydrochloric acid, phosphorus-pentachloride, and acetic acid (i. 4), show that it is an ethyl-compound, and may be represented by the formula $(C^2H^4)''\left\{\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}\right.$ or $\left.\begin{matrix}(C^2H^4)''\\(C^2H^5)^2\end{matrix}\right\}O^2$. The bivalent radicle C^2H^4 occurring in it is, however, not ethylene $\begin{matrix}CH^2\\|\\CH^2\end{matrix}$ (as in the isomeric compound ethylene diethylate), but ethylidene, $\begin{matrix}CH^3\\|\\CH\end{matrix}$. The constitutional formulæ of the two isomeric compounds are in fact:



$$\begin{matrix}CH^3\\|\\CH(OC^2H^5)^2\end{matrix}$$

Acetal.



$$\begin{matrix}CH^2(OC^2H^5)\\|\\CH^2(OC^2H^5)\end{matrix}$$

Ethylene Diethylate.

The three chlorinated derivatives of acetal are represented in like manner by the formulæ:

$$CH^2Cl.CH(OC^2H^5)^2;\ CHCl^2.CH(OC^2H^5)^2;\ CCl^3.CH(OC^2H^5)^2.$$

Dichloracetal, $C^6H^{12}Cl^2O^2$, is decomposed by zinc-ethyl at 140°, giving off a gaseous mixture of ethyl chloride, ethylene, and propylene, together with gases not absorbed by bromine (doubtless arising from the action of the ethyl chloride on the zinc-ethyl), and leaving ethyl oxide mixed with oxide and chloride of zinc. Neglecting the ethylene, which is formed as a secondary product in almost all re-actions of zinc-ethyl, the action may be represented by the equation:

$$\begin{aligned}&2[C^2H^2Cl^2.(OC^2H^5)^2] + 3Zn(C^2H^5)^2\\&= 2(C^2H^5)^2O + 2C^2H^5Cl + 4C^3H^6 + 2ZnO + ZnCl^2.\end{aligned}$$

(Paterno, Compt. rend. lxvii. 458.)

Trichloracetal, $C^6H^{11}Cl^3O^2$, is formed, together with dichloracetal, by the action of chlorine on alcohol at 80°. On treating the product with water, distilling the oil which collects at the bottom, redistilling the portion which boils above 185° in a current of steam, collecting apart the last fourth of the distillate, redistilling this in the same manner, and repeating these operations several times, a distillate of trichloracetal is at length obtained, which crystallises immediately in the receiver, and may be completely purified by pressure and recrystallisation from alcohol or ether. Trichloracetal crystallises in light shining needles, very much like caffeine. It melts at 72°, boils with slight decomposition at 230°, dissolves easily in alcohol and ether, and when heated with sulphuric acid to 150° yields chloral. (Paterno, Compt. rend. lxvii. 765.)

Methyl-acetal, $C^5H^{12}O^2 = (C^2H^4)''\left\{\begin{matrix}OC^2H^5\\OCH^3\end{matrix}\right.$, is produced, together with dimethyl-acetal (*infra*), by mixing in a capacious retort 300 pts. of sulphuric acid, 300 pts. of water, and 200 of manganese dioxide, then adding a mixture of 100 pts. alcohol and 90 pts. wood-spirit, and as soon as the first re-action is over, distilling till a quantity of liquid has passed over equal to that of the alcoholic mixture employed. The distillate is then rectified, the portions which distil above and below 68° being collected apart, and the distillation stopped at 85°. Each of the products thus obtained is purified by treating it with aqueous potash and with calcium chloride, as described under acetal (i. 3), and then rectified, the portions which pass over towards 65° in the one case and 85° in the other being collected apart.

Methyl-acetal is a very mobile colourless liquid having an odour like that of acetal, a specific gravity = 0·8535, and boiling at 85°. It burns with a brilliant flame, dissolves in all proportions of alcohol, in 15 parts of water, and is precipitated by water from its alcoholic solution. It is not decomposed by caustic potash.

The same or an isomeric compound has been found by Dancer in crude wood-spirit (iii. 1002).

Dimethyl-acetal, $C^4H^{10}O^2 = (C^2H^4)''\left\{\begin{matrix}OCH^3\\OCH^3\end{matrix}\right.$, is a colourless ethereal liquid, having an odour like that of methyl-compounds in general. Specific gravity = 0·8555. It boils at 65°, and burns with a luminous white blue-edged flame. (Wurtz, Ann. Ch. Phys. [3] xlviii. 373).

ACETAMIDE. C^2H^5NO.—This compound, heated in a sealed tube with an alkaline solution of *potassium permanganate*, yields no free nitrogen, and only a trace of ammonia, by far the greater portion of the nitrogen being oxidised to nitric or nitrous acid. (Wanklyn a. Gamgee, Chem. Soc. J. [2] vi. 25.)

Acetamide, heated in sealed tubes with saturated aqueous *hydriodic acid*, yields ammonia, acetic acid, and ethane or ethyl-hydride:

$$C^2H^5NO + H^2O + 3H^2 = C^2H^4O^2 + NH^3 + C^2H^6.$$

(Berthelot, Bull. Soc. Chim. [2] ix. 183.)

Acetamide, heated to about 210° with *carbon bisulphide*, gives off a number of gaseous products, among which are, hydrogen sulphide, carbon oxysulphide, carbon monoxide, and a combustible gas not absorbed by baryta or cuprous chloride, probably ethane, and leaves a residue of ammonium sulphocyanate mixed with undecomposed acetamide. The principal re-action appears to be:

$$2C^2H^5NO + CS^2 = NH^3.CHNS + COS + CO + C^2H^6.$$

(Ladenburg, Zeitschr. f. Chem. [2] v. 478.)

Acetamide forms a crystalline compound with *bitter almond oil*. (Strecker, Zeitschr. f. Chem. [2] iv. 651.) (See ALDEHYDES.)

ACETANILIDE. (See iv. 418; v. 1087.)

ACETENYL-BENZENE. $C^8H^6 = (C^6H^5) - C{\equiv}CH.$ – *Phenyl-acetylene* $C^2(C^6H^5)H.$ (Glaser, Zeitschr. f. Chem. v. 97.)—This hydrocarbon, related to acetylene in the same manner as cinnamene (styrol) to ethylene, is produced: 1. By heating phenyl-propiolic acid with water to 120° in a sealed tube:

$$\underset{\text{Phenyl-propiolic acid.}}{C^6H^5.C{\equiv}C.CO^2H} = CO^2 + \underset{\text{Acetenyl-benzene.}}{C^6H^5.C{\equiv}CH};$$

more easily by heating barium phenyl-propiolate mixed with sand to about 200°:

$$(C^6H^5.C{\equiv}C.CO^2)^2Ba + H^2O = CO^3Ba + CO^2 + 2(C^6H^5.C{\equiv}CH).$$

The copious yellow distillate thereby obtained is easily purified by a few distillations. The hydrocarbon is also formed in small quantity when phenyl-propiolic acid or either of its salts is simply boiled with water.

2. By the action of alcoholic potash on cinnamene dibromide, just as ethylene-dibromide similarly treated, yields acetylene as the final product:

$$C^2H^4Br^2 - 2HBr = C^2H^2;\quad C^8H^8Br^2 - 2HBr = C^8H^6.$$

The cinnamene dibromide is first converted by alcoholic potash into bromocinnamene, C^8H^7Br; and the latter is heated with the same re-agent to 120° in sealed tubes. The product distilled with water yields a distillate still containing alcohol, from which the acetenyl-benzene may be separated by water, and purified by drying with calcium chloride and rectification.

3. By heating methyl-benzylal chloride (produced by the action of phosphorus-pentachloride on methyl-benzoyl, $C^6H^5.COCH^3$) with very concentrated alcoholic potash to 120° in a sealed tube (Friedel, Zeitschr. f. Chem. [2] v. 123):

$$\underset{\text{Methyl-benzylal chloride.}}{C^6H^5.CCl^2CH^3} - 2HCl = \underset{\text{Acetenyl-benzene.}}{C^6H^5.C{\equiv}CH.}$$

Acetenyl-benzene is a frequent product of the decomposition of other hydrocarbons of the benzene series; thus it occurs in cinnamene which has been heated to redness in a stream of hydrogen; in that produced by the mutual action of benzene and ethylene at a red heat, or by the decomposition of ethyl-benzene; but not in the hydrocarbons of coal-tar. (Berthelot, Compt. rend. lxvii. 952.)

Acetenyl-benzene is a colourless strongly refracting liquid, having a peculiar aromatic odour, boiling constantly at 139°–140°, and having a vapour-density of 3·70 (calc. 3·53). It unites directly with bromine, forming a pungent oily liquid, and is quickly decomposed by nitric acid of specific gravity 1·35 and by sulphuric acid. With metallic solutions it forms precipitates analogous in composition to those of the other hydrocarbons of the acetylene series. Its alcoholic solution, mixed with an ammoniacal solution of *cuprous chloride* largely diluted with alcohol, forms a yellow precipitate of the compound $(C^6H^5.C^2)^2Cu.CuO$; the *silver compound* obtained in like manner is a light grey powder composed of $2(C^6H^5.C^2Ag).Ag^2O$. (Glaser.)

ACETIC ACID. *Hydrogen Acetate. Hydric Acetate.* $C^2H^4O^2 =$

$$= \begin{array}{l} CH^3 \\ | \\ COOH \end{array} = C\left\{\begin{array}{l} CH^3 \\ O'' \\ OH \end{array}\right. = \left.\begin{array}{c} CH^3CO \\ H \end{array}\right\}O = H.C^2H^3O^2. = C^2H^3O.OH.$$

Formation.—The chloride C^2H^3OCl corresponding to this acid is produced synthetically by passing a mixture of carbonyl chloride (phosgene gas) and marsh-gas through a retort heated to 120°:

$$COCl^2 + CH^4 = HCl + CH^3COCl;$$

and this chloride is converted by water into hydrochloric and acetic acids. (Harnitz-Harnitzky, Ann. Ch. Pharm. cxxxvi. 121.)

Acetic acid may be formed synthetically from acetylene (i.e. from carbon and hydrogen) by converting the latter into ethylene by direct addition of hydrogen, the ethylene into alcohol, and oxidising the alcohol. The transformation may, however, be more simply effected by heating acetylene dichloride with aqueous potash to 230° or with alcoholic potash to 100° for ten hours (Berthelot, Zeitschr. f. Chem. [2] v. 683):

$$C^2H^2Cl^2 + 3KHO = C^2H^3O^2K + 2KCl + H^2O.$$

Acetic acid is also produced, together with other products, by the fermentation of mucic acid in contact with yeast, white of egg, vegetable albumin, or most easily with muscular flesh:

$$2C^6H^{10}O^8 = 4C^2H^4O^2 + 4CO^2 + 2H^2.$$

Formation by oxidation of Alcohol.—Pasteur has shown by conclusive experiments that the formation of acetic acid from alcohol by atmospheric oxidation, in the ordinary process of vinegar making, depends essentially on the presence of a peculiar fungus, the *Mycoderma aceti.* The formation of vinegar from wine or beer is invariably preceded by the development of this fungus at the surface of the liquid. It appears to act by absorbing the oxygen of the air within its pores, like platinum-black, and thus bringing it into close contact with the particles of the alcohol. The plant may be sown on the surface of the liquid by introducing a small portion of it from another vinous liquid already in a state of acetous fermentation; or it may be introduced by simply exposing the liquid to the air, in which the germs of this fungus, as of many others, are always floating. But, like all other plants, it requires food for its development, and this it finds in the albuminous matter and mineral salts contained in ordinary vinous liquors. If these are absent the plant cannot grow, and acetification cannot take place. Thus, pure aqueous alcohol may be exposed to the air for any length of time without turning acid, because the germs of the mycoderm which fall into it from the air remain barren for want of nutriment; but as soon as any albuminous matter is introduced into the liquid, the plant begins to grow and the alcohol is oxidised. The albuminous matter is not, however, itself the active agent in the change, and is quite incapable of inducing it in the absence of the fungus. I a bottle, partly filled with wine and containing air in its ordinary state, be hermeticall closed and then heated to a temperature of 55° or upwards, the germs of the myco derm present in the air or in the liquid will be killed, and under these conditions th wine may be kept for years without exhibiting the slightest degree of acetificatio although it contains an abundance of albuminous matter; but if it be opened, and th liquid exposed to the air, so that the germs of the fungus may have access to it, th formation of acetic acid will take place. Moreover, pure aqueous alcohol may acetified without the aid of any albuminous matter, provided the mycoderm ha access to it, and be supplied with the nitrogen and saline matters necessary for i growth. Pasteur has in fact shown that this nutriment may be supplied in the fo of alkaline and earthy phosphates and ammonium phosphate, the latter furnishi the nitrogen. Under these circumstances the mycoderm grows, though less quic than in ordinary vinous liquids, and the alcohol is slowly converted into acetic acid

The acetification goes on most quickly and favourably when the mycoderm gr only at the surface of the liquid; if it sinks to the bottom or diffuses itself thro the mass of the liquid, the oxygen contained in its pores acts upon the acetic already formed, and burns it completely to carbonic acid and water: in this wa the mycoderm be allowed to remain in the liquid after the acetification is complete, whole of the acetic acid may be destroyed and the liquid rendered perfectly neu (Pasteur, *Études sur le Vinaigre,* Paris, 1868; also *Annales scientifiques de l'I normale supérieure,* tome i. 1864; Bull. Soc. Chim. 1861, p. 94; Jahresb. 1 p. 786.)

On the formation of acetic acid in alcoholic fermentation, see also Béchamp (Chim. pure, v. 575; Jahresb. 1863, p. 773); Blondeau (Compt. rend. lvii. Jahresb. 1864, p. 312).

Physical Properties.—According to Mendelejef (Jahresb. 1863, p. 7), the sp. glacial acetic acid at 15° (referred to water at 4° as unity) is 1·0607. Accordi Régnault (*Relation des expériences,* &c., p. 751, Jahresb. 1863, p. 74), glacial acid may remain solid at + 16°, but, when once liquefied, is very difficult to re-solidify, sustaining without change a temperature of − 8° or even − 10°, in spite of brisk agitation; but contact with a pointed piece of glass, or better, with a crystal of the glacial acid, causes it to solidify immediately. Oudemans (Zeitschr. f. Chem. 1866, p. 750; Jahresb. 1866, p. 300) prepared pure acetic acid by rectifying the commercial glacial acid over manganese peroxide and sodium acetate, then subjecting it to fractional distillation and crystallisation, till it exhibited a constant specific gravity. This sp. gr. was 1·05538 at 15°. The acid melted at 16·45°, and boiled at 117° (bar. at 763 mm.); after a fourth of the liquid had passed over, the boiling point rose to 117·6°, and finally (in the last ⅛th of the distillate) to 118·2°.

From determinations of the sp. gr. of mixtures of acetic acid vapour and hydrogen gas at various temperatures, Playfair and Wanklyn (Chem. Soc. J. xv. 153) infer that the vapour of acetic acid probably has, at comparatively high temperatures, a density of 2·073 referred to air, or 30 referred to hydrogen, corresponding to a condensation of 2 volumes for the molecule $C^2H^4O^2$, and at lower temperatures, the density 60 (referred to hydrogen), corresponding to a similar condensation for the molecule $C^4H^8O^4$; further, that the constitution of the molecule is probably different at these different temperatures. Cahours had formerly shown (i. 10) that the vapour of acetic acid begins to exhibit its normal density at about 240°. From recent experiments he concludes that it still retains this density at 350°, and begins to exhibit a lower density only at 440°, being then partially decomposed into marsh gas and carbon dioxide: hence the normal density remains constant for an interval of about 200°.

Oxidation by Potassium Permanganate.—Acetic acid appears at first to have no action on a solution of the permanganate, either acid or alkaline. Nevertheless, on heating acetic acid with a dilute neutral solution of the permanganate to 100° in a long-necked flask, a reaction is soon set up and becomes considerable after 15 or 20 hours: the only products are water and carbonic acid. Sodium acetate, left in contact in the cold with a neutral solution of the permanganate, does not exhibit any reaction for the first few days, but at the end of three months a visible reduction takes place, attended with formation of carbonate. At the boiling heat the reduction becomes visible after a few hours, especially in presence of a small quantity of potash, resulting in the formation of oxalic acid: $C^2H^4O^2 + O^3 = C^2H^2O^4 + H^2O$. (Berthelot, Bull. Soc. Chim. [2] viii. 392.)

According to F. Lossen (Ann. Ch. Pharm. cxiv. 174), acetic acid may be converted into oxalic acid by dissolving 1 pt. sodium acetate, 1 pt. sodium hydrate, and 2 pts. potassium permanganate in a small quantity of water, boiling the solution to dryness, and heating the dry mass to a temperature not sufficient to decompose potassium oxalate, till a sample no longer forms a green solution with water.

Aqueous Acetic Acid.—It was formerly supposed that a mixture of glacial acetic acid and water exhibits a maximum amount of condensation when the proportions are such as to form the hydrate $C^2H^4O^2.H^2O$, containing 77 per cent. of the glacial acid to 23 of water; and that this hydrate boils without decomposition at a constant temperature. Results tending to confirm this statement have been published by Bussy and Buignet (Jahresb. 1865, p. 69). On the other hand, Roscoe has shown (Chem. Soc. J. xv. 270) that aqueous acetic acid of this, as well of any other strength, suffers decomposition by boiling, and that, in whatever proportions glacial acetic acid and water may be mixed, the mixture may be decomposed by distillation, under either ordinary or increased pressure, in such a manner as ultimately to leave a residue of glacial acetic acid;—in short, that there is no such thing as a definite hydrate of acetic acid. From Roscoe's determinations, which agree very nearly with those of Van Toorn (J. für Chem. vi. 171), of the density of aqueous acetic acid of strengths a little above and below that of the supposed hydrate $C^2H^4O^2.H^2O$, it further appears that there is no maximum density corresponding to a definite strength, but that aqueous acids of strengths varying from 76·5 to 80 per cent. exhibit the same density:

Percentage of acid . . .	76·5°	77·5°	79°	80°	98·5°	100°
Sp. gr. at 15·5°	1·0752	1·0754	1·0754	1·0754	1·0597	1·0954

The recent experiments of Oudemans, made with acetic acid purified in the manner above described, likewise show that the maximum density of mixtures of acetic acid and water bears no relation whatever to a fixed equivalent proportion of the acid and water, but corresponds to a different proportion for each particular temperature. Oudemans' results for the temperatures 0°, 15°, and 40°, are given in the following table: they agree nearly with the older determinations by Van Toorn, but not with those of Mohr (i. 11), which, according to Oudemans, appear to have been made, not with pure glacial acetic acid, but with an acid containing 5 per cent. of water.

Density of Aqueous Acetic Acid (Oudemans).

Per cent.	Density at 0°	Density at 15°	Density at 40°	Per cent.	Density at 0°	Density at 15°	Density at 40°
0	0·9999	0·9992	0·9924	51	1·0740	1·0623	1·0416
1	1·0016	1·0007	0·9936	52	1·0749	1·0631	1·0423
2	1·0033	1·0022	0·9948	53	1·0758	1·0638	1·0429
3	1·0051	1·0037	0·9960	54	1·0767	1·0646	1·0434
4	1·0069	1·0052	0·9972	55	1·0775	1·0653	1·0440
5	1·0088	1·0067	0·9984	56	1·0783	1·0660	1·0445
6	1·0106	1·0083	0·9996	57	1·0791	1·0666	1·0450
7	1·0124	1·0098	1·0008	58	1·0798	1·0673	1·0455
8	1·0142	1·0113	1·0020	59	1·0806	1·0679	1·0460
9	1·0159	1·0127	1·0032	60	1·0813	1·0685	1·0464
10	1·0176	1·0142	1·0044	61	1·0820	1·0691	1·0468
11	1·0194	1·0157	1·0056	62	1·0826	1·0697	1·0472
12	1·0211	1·0171	1·0067	63	1·0832	1·0702	1·0475
13	1·0228	1·0185	1·0079	64	1·0838	1·0707	1·0479
14	1·0245	1·0200	1·0090	65	1·0845	1·0712	1·0482
15	1·0262	1·0214	1·0101	66	1·0851	1·0717	1·0485
16	1·0279	1·0228	1·0112	67	1·0856	1·0721	1·0488
17	1·0295	1·0242	1·0123	68	1·0861	1·0725	1·0491
18	1·0311	1·0256	1·0134	69	1·0866	1·0729	1·0493
19	1·0327	1·0270	1·0144	70	1·0871	1·0733	1·0495
20	1·0343	1·0284	1·0155	71	1·0875	1·0737	1·0497
21	1·0359	1·0298	1·0166	72	1·0879	1·0740	1·0498
22	1·0374	1·0311	1·0176	73	1·0883	1·0742	1·0499
23	1·0390	1·0324	1·0187	74	1·0886	1·0744	1·0500
24	1·0405	1·0337	1·0197	75	1·0888	1·0746	1·0501
25	1·0420	1·0350	1·0207	76	1·0891	1·0747	1·0501
26	1·0435	1·0363	1·0217	77	1·0893	1·0748	1·0501
27	1·0450	1·0375	1·0227	78	1·0894	1·0748	1·0500
28	1·0465	1·0388	1·0236	79	1·0896	1·0748	1·0499
29	1·0479	1·0400	1·0246	80	1·0897	1·0748	1·0497
30	1·0493	1·0412	1·0255	81	1·0897	1·0747	1·0495
31	1·0507	1·0424	1·0264	82	1·0897	1·0746	1·0492
32	1·0520	1·0436	1·0274	83	1·0896	1·0744	1·0489
33	1·0534	1·0447	1·0283	84	1·0894	1·0742	1·0485
34	1·0547	1·0459	1·0291	85	1·0892	1·0739	1·0481
35	1·0560	1·0470	1·0300	86	1·0889	1·0736	1·0475
36	1·0573	1·0481	1·0308	87	1·0885	1·0731	1·0469
37	1·0585	1·0492	1·0316	88	1·0881	1·0726	1·0462
38	1·0598	1·0502	1·0324	89	1·0876	1·0720	1·0455
39	1·0610	1·0513	1·0332	90	1·0871	1·0713	1·0447
40	1·0622	1·0523	1·0340	91		1·0705	1·0438
41	1·0634	1·0533	1·0348	92		1·0696	1·0428
42	1·0646	1·0543	1·0355	93		1·0686	1·0416
43	1·0657	1·0552	1·0363	94		1·0674	1·0403
44	1·0668	1·0562	1·0370	95		1·0660	1·0388
45	1·0679	1·0571	1·0377	96		1·0644	1·0370
46	1·0690	1·0580	1·0384	97		1·0625	1·0350
47	1·0700	1·0589	1·0391	98		1·0604	1·0327
48	1·0710	1·0598	1·0397	99		1·0580	1·0301
49	1·0720	1·0607	1·0404	100		1·0553	1·0273
50	1·0730	1·0615	1·0410				

ACETATES (METALLIC).—These salts are represented by the following formulæ, according to the equivalent value of the metal which they contain:

For monatomic or univalent metals (sodium) $NaC^2H^3O^2$ or $\left.\begin{matrix}C^2H^3O\\ Na\end{matrix}\right\}O$

For diatomic or bivalent metals (barium) $Ba''(C^2H^3O^2)^2$ or $\left.\begin{matrix}(C^2H^3O)^2\\ Ba''\end{matrix}\right\}O^2$

For trivalent metals (thallium in thallic salts) $Th'''(C^2H^3O^2)^3$ or $\left.\begin{matrix}(C^2H^3O)^3\\ Tl'''\end{matrix}\right\}O^3$

For (apparently) trivalent metals (iron) $(Fe^2)^{vi}(C^2H^3O^2)^6$ or $\left.\begin{matrix}(C^2H^3O)^6\\ (Fe^2)^{vi}\end{matrix}\right\}O^6$.

In the last case the metal is really tetratomic (iron, chromium, aluminium), but when two of its atoms are associated together, one unit of equivalence in each of them is neutralised by combination with the other, so that the group is really sexvalent like the group C^2 in ethyl hydride, C^2H^6; thus the formula of neutral ferric acetate may be written thus:

$$\begin{array}{l}Fe'''(C^2H^3O^2)^3\\ |\\ Fe'''(C^2H^3O^2)^3.\end{array}$$

In acetates containing bivalent or multivalent metals, one or more equivalents of the radicle, C^2H^3O, may be replaced by chlorine or bromine, or by other acid radicles or residues, such as NO^3, $(SO^4)''$, &c., e.g.,

Barium aceto-nitrate * . . . . $Ba''\left\{\begin{matrix}C^2H^3O^2\\ NO^3\end{matrix}\right.$

Chromic diaceto-tetrachloride . . . . . . $(Cr^2)^{vi}\left\{\begin{matrix}(C^2H^3O^2)^2\\ Cl^4\end{matrix}\right.$

Ferric tetraceto-dinitrate . . . . $(Fe^2)^{vi}\left\{\begin{matrix}(C^2H^3O^2)^4\\ (NO^3)^2\end{matrix}\right.$;

partly also, in some cases, by hydroxyl, HO, forming basic salts, e.g.,

Ferric tetracetate . . . . $(Fe^2)^{vi}\left\{\begin{matrix}(C^2H^3O^2)^4\\ (HO)^2\end{matrix}\right.$

Ferric triaceto-dinitrate . . . . $(Fe^2)^{vi}\left\{\begin{matrix}(C^2H^3O^2)^3\\ (NO^3)^2\\ HO.\end{matrix}\right.$

Cerous Acetate, $Ce''(C^2H^3O^2)^2$ + aq., obtained by dissolving cerous oxide or carbonate in acetic acid, or by decomposing cerous sulphate with barium acetate, crystallises in radiate groups of small needles, which give off their water in dry air without losing their crystalline form; after drying at 115°, they become carbonised at a higher temperature, without fusing, and when ignited leave a residue of cerosoceric oxide (Lange, *J. pr. Chem.* lxxxii. 129). According to Czudnowicz (*ibid.* lxxxii. 217; *Jahresb.* 1861, p. 190), the water of crystallisation cannot be expelled without decomposition of the salt, which in fact begins at a temperature a little above 100°, the salt caking together, and ultimately leaving cerosoceric oxide.

Chromic Acetates. The *normal salt*, $Cr^2(C^2H^3O^2)^6$ + 2aq., is obtained as a green crystalline mass, by evaporating a solution of chromic hydrate in acetic acid. It is insoluble in alcohol. Its aqueous solution, which is green by reflected, red by transmitted light, is not decomposed, either by ebullition or by addition of lime-water; but ammonia throws down from it a green precipitate of chromic hydrate, soluble in excess of the reagent. (H. Schiff, *Ann. Ch. Phys.* [3] lxxi. 140; Schützenberger, *Bull. Soc. Chim.* 1865, iv. 86.)

The solution of the normal acetate heated for several days with excess of chromic hydrate, loses its acid reaction and yields by evaporation a green powder soluble in water, consisting of a basic acetate, $Cr^2\left\{\begin{matrix}(C^2H^3O^2)^4\\ (HO)^2\end{matrix}\right.$. (Schiff.)

Chromic Diacetotetrachloride, $Cr^2\left\{\begin{matrix}(C^2H^3O^2)^2\\ Cl^4.\end{matrix}\right.$ + 4aq., is obtained by dissolving chromic dioxytetrachloride (chlorochromic acid), $Cr^{vi}O^2Cl^2$, in strong acetic acid. It is an unstable salt, which gives off acetic acid when heated above 100°. The chlorine is but very slowly precipitated from it by silver nitrate at ordinary temperatures, but, on the other hand, the salt easily yields acetic ether when heated with sulphuric acid and alcohol. (Schiff.)

Chromic Diaceto-sulphate, $Cr^2\left\{\begin{matrix}(C^2H^3O^2)^2\\ (SO^4)^2\end{matrix}\right.$, obtained by dissolving chromic disulphate in acetic acid, is a crystalline salt which becomes anhydrous at 100°, and gives off acetic acid at a higher temperature. (Schiff.)

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* Described vol. iv. p. 90.

Chromic Pentaceto-nitrate, $\mathrm{Cr}^2\left\{\begin{matrix}(\mathrm{C}^2\mathrm{H}^3\mathrm{O}^2)^5\\ \mathrm{NO}^3\end{matrix}\right.$ + 2aq., is obtained by mixing a solution of chromic hydrate in a slight excess of acetic acid with a solution of the same quantity of chromic hydrate in the exact quantity of nitric acid required to dissolve it. The concentrated solution, when left to itself, deposits an abundant crystallisation of a dark green salt, which may be purified by recrystallisation from water or from glacial acetic acid. It forms dark green bulky laminæ, which give off nitrous fumes at 100°, the chromium being at the same time converted into trioxide (Schützenberger).

Ferric Acetates. The *normal salt*, $(\mathrm{Fe}^2)^{\mathrm{vi}}(\mathrm{C}^2\mathrm{H}^3\mathrm{O}^2)^6$ or $\left.\begin{matrix}(\mathrm{C}^2\mathrm{H}^3\mathrm{O})^6\\ (\mathrm{Fe}^2)^{\mathrm{vi}}\end{matrix}\right\}\mathrm{O}^6$, is described at p. 16, vol. i. The following basic acetates are known:—

Ferric Tetracetate, $\mathrm{Fe}^2\left\{\begin{matrix}(\mathrm{C}^2\mathrm{H}^3\mathrm{O}^2)^4\\ (\mathrm{HO})^2\end{matrix}\right.$, is obtained by dissolving at 50° the ferric hydrate produced from 1 part of iron, in 10 parts of acetic acid of 30 per cent., and evaporating the solution at 70°. It is an amorphous mass, soluble in alcohol and in water. (Oudemans, *Jahresber*. 1858, p. 282.)

Ferric Triacetate, $\mathrm{Fe}^2\left\{\begin{matrix}(\mathrm{C}^2\mathrm{H}^3\mathrm{O}^2)^3\\ (\mathrm{HO})^3\end{matrix}\right.$, is probably contained in the red solution obtained by treating ferric dichlorotriacetate (*infra*) with silver oxide. This solution, evaporated in a vacuum, becomes syrupy, but does not crystallise. It quickly decomposes at ordinary temperatures, forming an ochreous jelly. (Scheurer-Kestner.)

Triferric Diacetate. $\mathrm{Fe}^2\left\{\begin{matrix}(\mathrm{C}^2\mathrm{H}^3\mathrm{O}^2)^2\\ (\mathrm{HO})^4\end{matrix}\right..2\mathrm{Fe}^2\mathrm{O}^3$.—This is the ochreous deposit formed when a solution of ferrous acetate is exposed to the air.

Other basic salts appear to be formed in the decomposition of the normal salt by heat or otherwise, but they have not been analysed.

Ferric Aceto-nitrates. (Scheurer-Kestner, *Ann. Ch. Phys.* [3] lxiii. 422; lxviii. 472; *Jahresber*. 1861, p. 307.)—These salts, which may be produced by mixing the solutions of ferric nitrate and acetate in various proportions, or by dissolving ferric hydrate in various mixtures of nitric and acetic acids, are mostly very unstable: on boiling them with water, ferric oxide is precipitated, and the acids are set free.

The *tetraceto-dinitrate*, $\mathrm{Fe}^2\left\{\begin{matrix}(\mathrm{C}^2\mathrm{H}^3\mathrm{O}^2)^4\\ (\mathrm{NO}^3)^2\end{matrix}\right.$ + 6aq., is prepared: *α*. By heating a solution of ferrous acetate (sp. gr. 1·250) mixed with excess of acetic acid to 80°, then adding nitric acid by drops, and leaving the solution to cool:

$$6\mathrm{Fe}''(\mathrm{C}^2\mathrm{H}^3\mathrm{O}^2)^2 + 8\mathrm{HNO}^3 = 3(\mathrm{Fe}^2)^{\mathrm{vi}}\left\{\begin{matrix}(\mathrm{C}^2\mathrm{H}^3\mathrm{O}^2)^4\\ (\mathrm{NO}^3)^2\end{matrix}\right. + 2\mathrm{NO} + 4\mathrm{H}^2\mathrm{O}.$$

β. By dissolving ferric dinitrate in acetic acid:

$$(\mathrm{Fe}^2)^{\mathrm{vi}}\left\{\begin{matrix}(\mathrm{NO}^3)^2\\ (\mathrm{HO})^4\end{matrix}\right. + 4\mathrm{C}^2\mathrm{H}^4\mathrm{O}^2 = (\mathrm{Fe}^2)^{\mathrm{vi}}\left\{\begin{matrix}(\mathrm{C}^2\mathrm{H}^3\mathrm{O}^2)^4\\ (\mathrm{NO}^3)^2\end{matrix}\right. + 4\mathrm{H}^2\mathrm{O}.$$

The reaction is terminated when the mixture no longer yields a precipitate with nitric acid.

γ. By dissolving 1 molecule of ferric hydrate in 4 mol. acetic acid and 2 mol. nitric acid.—*δ*. By mixing 1 mol. ferric nitrate with 2 mol. ferric acetate.—*ε*. By treating ferric dichloro-tetracetate (*infra*) with silver nitrate.

This salt crystallises in well-defined right rhombic prisms, having a blood-red colour, very soluble in water, soluble in all proportions of alcohol, insoluble in ether, which may therefore be used for washing the crystals. It is decomposed by the slightest elevation of temperature, and when treated with nitric acid, yields ferric tetraceto-nitrate (*infra*).

The *diaceto-tetranitrate*, $\mathrm{Fe}^2\left\{\begin{matrix}(\mathrm{C}^2\mathrm{H}^3\mathrm{O}^2)^2\\ (\mathrm{NO}^3)^4\end{matrix}\right.$ + 8aq., is obtained: *α*. By leaving a solution of ferric tetranitrate, $\mathrm{Fe}^2(\mathrm{NO}^3)^4(\mathrm{HO})^2$ (sp. gr. 1·250), mixed with excess of strong acetic acid to evaporate in a vacuum, and washing the resulting crystals with ether containing alcohol.—*β*. By dissolving 1 mol. ferric hydrate in 2 mol. acetic and 4 mol. nitric acid.—*γ*. By mixing 1 mol. normal ferric acetate with 2 mol. ferric nitrate. It crystallises in small oblique rhombic prisms, often united in crosses.

The *triaceto-dinitrate*, $(\mathrm{Fe}^2)^{\mathrm{vi}}\left\{\begin{matrix}(\mathrm{C}^2\mathrm{H}^3\mathrm{O}^2)^3\\ (\mathrm{NO}^3)^2\\ \mathrm{HO}\end{matrix}\right.$ + 8aq., is prepared by treating ferric hydrate with proportional quantities of the two acids; or by treating ferric triaceto-dichloride (*infra*) with silver nitrate. It forms dark-coloured, almost black, rhomboidal crystals or crystalline plates, soluble in alcohol.

The *tetraceto-nitrate*, $\mathrm{Fe^2}\left\{\begin{matrix}\mathrm{(C^2H^3O^2)^4}\\ \mathrm{NO^3}\\ \mathrm{HO}\end{matrix}\right. + 4\mathrm{aq.}$, is obtained by digesting a mixture of 1 mol. ferric hydrate, 4 mol. acetic acid, and 1 mol. nitric acid at 40° for several days, and evaporating in a vacuum; the same result is obtained with a mixture of 1 mol. ferric acetate, 1 mol. ferric dinitrate, and 1 mol. acetic acid. It forms right rhombic prisms, of red-brown colour; hard, shining, less deliquescent than the other ferric aceto-nitrates, very soluble in water and in alcohol, decomposible by slight rise of temperature.

The *triaceto-nitrate*, $\mathrm{Fe^2}\left\{\begin{matrix}\mathrm{(C^2H^3O^2)^3}\\ \mathrm{NO^3}\\ \mathrm{(HO)^2}\end{matrix}\right. + \mathrm{aq.}$, is prepared by digesting a mixture of ferric hydrate and the two acids in the required proportions at about 30°; or by frequently agitating a mixture of 2 mol. acetic acid and 1 mol. ferric dinitrate; the product in the latter case is a mixture of triaceto-nitrate and tetra-nitrate. The triaceto-nitrate forms flattened monoclinic prisms of deep-red colour, very soluble in water and in alcohol, insoluble in ether.

Ferric Diformo-diaceto-nitrate. $\mathrm{Fe^2}\left\{\begin{matrix}\mathrm{(CHO^2)^2}\\ \mathrm{(C^2H^3O^2)^2}\\ \mathrm{NO^3}\\ \mathrm{HO}\end{matrix}\right. + 5\mathrm{aq.}$—This salt may be prepared by the direct action of the three acids in proportional quantities on ferric hydrate; but more advantageously by the slow action of nitric acid (sp. gr. = 1·38) on a mixture of ferrous acetate and formate at the heat of the water-bath. When the oxidation is complete, a red liquid is obtained, which is very unstable, but crystallises when evaporated to a syrup over oil of vitriol. It is very soluble in water and in alcohol, insoluble in ether; very unstable, depositing ferric oxide on boiling, and decomposing if the evaporation of the solution be carried too far, even in a vacuum.

The quantity of nitric acid required to effect the oxidation of the ferrous salt in the process of preparation just described, is double of that required by the formula of the salt: hence it is probable that the salt $\mathrm{Fe^2}\left\{\begin{matrix}\mathrm{(CHO^2)^2}\\ \mathrm{(C^2H^3O^2)^2}\\ \mathrm{(NO^3)^2}\end{matrix}\right.$ is first formed and afterwards converted into the basic salt just described by loss of nitric peroxide; red vapours are in fact disengaged during the evaporation of the mixture.

Ferric Aceto-chlorides.—The *triaceto-chloride*, $\mathrm{(Fe^2)^{vi}}\left\{\begin{matrix}\mathrm{(C^2H^3O^2)^3}\\ \mathrm{Cl^2}\\ \mathrm{HO}\end{matrix}\right. + 3\mathrm{aq.}$, is obtained by cautiously treating with nitric acid a solution of ferrous chloride in acetic acid heated to 80°.

$$12\mathrm{Fe''Cl^2} + 9\mathrm{C^2H^4O^2} + 4\mathrm{NO^3H} = 3\mathrm{(Fe^2)^{vi}}\left\{\begin{matrix}\mathrm{(C^2H^3O^2)^3}\\ \mathrm{Cl^2}\\ \mathrm{HO}\end{matrix}\right. + 3\mathrm{Fe^2Cl^6} + 4\mathrm{NO} + 5\mathrm{H^2O}.$$

The same salt is formed when a mixture of 1 mol. ferric hydrate, 2 mol. acetic acid, and 1 mol. hydrochloric acid is digested at 40° for two or three days. It forms very hard crystals, black by reflected, red by transmitted light, very soluble in alcohol and in water. When treated with silver oxide, they yield ferric triacetate. (Scheurer-Kestner, *Ann. Ch. Phys.* [3] lxviii. 472; *Jahresb.* 1863, p. 257.)

The *tetraceto-dichloride*, $\mathrm{(Fe^2)^{vi}}\left\{\begin{matrix}\mathrm{(C^2H^3O^2)^4}\\ \mathrm{Cl^2}\end{matrix}\right. + 3\mathrm{aq.}$, is obtained by dissolving 1 mol. ferric hydrate in a mixture of 2 mol. hydrochloric and 4 mol. acetic acid; or by oxidising ferrous chloride dissolved in very strong acetic acid with nitric acid. It forms yellowish-red crystals, soluble in alcohol and in water, easily resolved into acetic acid and ferric triaceto-dichloride. When treated with silver nitrate, it decomposes after 12 hours at 50°, forming ferric tetraceto-dinitrate:

$$\mathrm{Fe^2}\left\{\begin{matrix}\mathrm{(C^2H^3O^2)^4}\\ \mathrm{Cl^2}\end{matrix}\right. + 2\mathrm{AgNO^3} = 2\mathrm{AgCl} + \mathrm{(Fe^2)^{vi}}\left\{\begin{matrix}\mathrm{(C^2H^3O^2)^4}\\ \mathrm{(NO^3)^2}\end{matrix}\right.$$

Lead Acetates, or Plumbic Acetates. According to J. Löwe (*J. pr. Chem.* xcviii. 385; *Jahresb.* 1866, p. 235), there are only three definite plumbic acetates, viz.,

The normal or monoplumbic salt . .	$\mathrm{Pb''(C^2H^3O^2)^2}$
The bibasic or biplumbic salt . .	$\overset{''}{\mathrm{Pb}}{}^2\left\{\begin{matrix}\mathrm{(C^2H^3O^2)^2}\\ \mathrm{O''}\end{matrix}\right.$ or $\mathrm{Pb''(C^2H^3O^2)^2.Pb''O}$
The tribasic or triplumbic salt . .	$\overset{''}{\mathrm{Pb}}{}^3\left\{\begin{matrix}\mathrm{(C^2H^3O^2)^2}\\ \mathrm{O^2}\end{matrix}\right.$ or $\mathrm{Pb''(C^2H^3O^2)^2.2Pb''O}$.

When bromine is added to a solution of the monoplumbic salt, a brown precipitate of lead dioxide is produced, and if the liquid be warmed, the formation of this precipitate goes on till the bromine has been added in the proportion of 2 at. Br to 2 mol. $(C^2H^3O^2)^2Pb$. The solution contains lead bromide and acetic acid:

$$2(C^2H^3O^2)^2Pb + 2H^2O + Br^2 = PbO^2 + PbBr^2 + 4C^2H^4O^2.$$

(Chapman a. Smith, *Chem. Soc. J.* [2] vii. 185.)

The *biplumbic salt*, which dissolves easily in water and in alcohol of 90 p. c., is produced by treating 1 mol. lead-oxide with a solution of at least 1 mol., or an excess, of the normal salt; also when the triplumbic salt is dissolved in the solution of the monoplumbic salt; and by the incomplete decomposition of the monoplumbic salt with aqueous ammonia, potash, or soda. Ammonia added in excess to its aqueous solution, throws down a mixture of triplumbic acetate and plumbic hydrate:

$$4Pb^2\left\{\begin{matrix}(C^2H^3O^2)^2\\O\end{matrix}\right. + 4NH^3 + 3H^2O = 2Pb^3\left\{\begin{matrix}(C^2H^3O^2)^2\\O^2\end{matrix}\right. + Pb^2H^2O^3 + 4(NH^4)(C^2H^3O^2).$$

The *triplumbic salt* is also produced: *a.* When a solution of the normal salt (1 mol.) is digested with at least 2 mol. of pure plumbic oxide (of crude litharge, about 3 mol. are required). By prolonged digestion of 6 pts. normal acetate (1 mol.) with 30 pts. water and 7 pts. (2 mol.) of good finely pulverised litharge, till the undissolved residue appeared perfectly white, Löwe obtained a solution containing chiefly the biplumbic salt, while the spongy residue consisted chiefly of the triplumbic acetate and plumbic carbonate. When 6 pts. of the normal salt were digested with 14 pts. (4 mol.) of litharge, the solution contained the triplumbic salt; and the crystalline deposit, which dissolved partially in boiling water, leaving a considerable quantity of plumbic oxide and carbonate, was likewise found to contain the triplumbic, but no sexplumbic salt.—*β.* The triplumbic salt is further produced by cautious addition of potash to the solution of the normal salt, and by mixing the solution of the latter with excess of ammonia. It is obtained in silky needles when 100 cc. of the cold saturated solution of the normal salt are mixed with 100 cc. water, the mixture poured into 40 to 50 cc. of aqueous ammonia (of what strength?), and the whole warmed over the water-bath in a vessel which protects it from the air. If the solution of the normal salt be mixed with only ⅕th of its volume of aqueous ammonia, the biplumbic salt is formed in solution, together with a precipitate of triplumbic salt; with less than ⅕th volume of aqueous ammonia, only the biplumbic salt is formed. The triplumbic salt treated with ammonia, either at ordinary or at higher temperatures, is not converted into a sexbasic salt, but partially decomposed, with separation of crystalline plumbic hydrate, or yellow plumbic oxide; neither is it converted into a more basic compound by digesting it with plumbic oxide (which in fact is not at all attacked by it). In its aqueous solution, caustic potash forms a precipitate of plumbic hydrate ($Pb^2H^2O^3$ dried at 100°).

From all these results, Löwe concludes that the sexbasic salt commonly said to be formed by agitating a solution of the diplumbic or triplumbic salt with lead oxide, has no existence. Neither did he succeed in preparing the sesquibasic salt (i. 16). When the dehydrated normal salt is heated to 200°, till the fused mass resolidifies, the residue dissolves easily in cold water, leaving a mixture of plumbic oxide and carbonate, and the solution contains biplumbic acetate, together with more or less of the triplumbic salt (precipitable by strong alcohol), according to the duration of the heating.

The composition of the basic lead acetates above described was inferred from the mode of their decomposition with potassium nitrate, whereby the corresponding basic nitrates are supposed to be formed, which by their sparing solubility and permanence are well adapted for quantitative estimation. Thus a basic lead acetate was inferred to be biplumbic or triplumbic when its solution gave with potassium nitrate a precipitate of biplumbic or triplumbic nitrate.

For the preparation of officinal sub-acetate of lead, or lead-vinegar (if it is to contain the biplumbic salt), Löwe recommends that 2 pts. of the triplumbic salt precipitated by ammonia, and well pressed, be dissolved at a gentle heat in a solution of 1 pt. of the crystallised normal salt in 4 or 5 pts. of water thoroughly de-aërated by boiling.

Acetates of Mercury. The formulæ of these salts, according to the atomic weight of mercury now adopted, are:

Mercurous acetate $\left.\begin{matrix}Hg(C^2H^3O^2)\\Hg(C^2H^3O^2)\end{matrix}\right\}(C^2H^3O^2)^2$

Mercuric acetate $Hg''(C^2H^3O^2)^2$.

Mercuric acetosulphide, $Hg''(C^2H^3O^2)^2.Hg''S$, is produced by passing hydrogen sulphide into a concentrated solution of mercuric acetate. The mercuric sulphide thereby produced dissolves at first in the mercuric acetate, but on passing the gas in excess the acetosulphide is precipitated as a white crystalline powder, and ultimately the whole is converted into black mercuric sulphide. The crystalline acetosulphide may be obtained in extremely thin, flexible, nacreous, translucent, rectangular plates, by adding recently precipitated mercuric sulphide to a warm concentrated solution of mercuric acetate, as long as it continues to turn white and assume a crystalline aspect,—mixing the filtered solution with an equal volume of alcohol of 90° and a little strong acetic acid, and leaving it for two or three days in a cool dark place. The compound dissolves in 12 parts of warm water, and decomposes on boiling, with deposition of mercuric sulphide and basic mercuric acetate. Alcohol and ether, at the boiling heat, dissolve out almost all the acetic acid. A solution of recently precipitated mercuric sulphide in mercuric acetate yields with soluble chlorides a white precipitate of the sulphochloride $Hg^3S^2Cl^2$ or $2HgS.HgCl^2$, and precipitates of analogous composition with soluble bromides and iodides and alkaline nitrates; with alkaline sulphates a precipitate of sulphato-sulphide, containing $HgS.2HgSO^4$; with chromic acid and alkaline chromates, an ochre-coloured precipitate of the chromato-sulphide, $HgS.2HgCrO^4$. (R. Palm, *Chem. Centralb.* 1863, pp. 118, 121, 175, 227; *Jahresb.* 1862, p. 220.)

Potassium Acetate. $C^2H^3O^2K$.—When this salt is heated for some hours in a sealed tube with *bromine* and water in the proportion of 2 at. bromine to 1 mol. $C^2H^3O^2K$, potassium bromide is formed, and on opening the tube, carbon dioxide escapes, together with a gas which burns with a green flame: probably methyl-bromide:

$$C^2H^3O^2K + Br^2 = KBr + CO^2 + CH^3Br.$$

Traces of a heavy liquid insoluble in water, probably brominated methyl-bromide, are also formed. The same reaction takes place very quickly under the influence of direct sunshine. *Chlorine* acts in a similar manner, one of the products formed by it being methylene dichloride CH^2Cl^2. (Chapman a. Smith, *Chem. Soc. J.* [2] vii. 185.)

Silver Acetate. This salt is resolved by heat into crystalline hydrogen acetate, carbon dioxide, marsh gas, and a residue of metallic silver and charcoal:

$$4C^2H^3O^2Ag = 3C^2H^4O^2 + CO^2 + Ag^4 + C;\ \text{and}\ C^2H^4O^2 = CH^4 + CO^2.$$

Heated with *iodine*, in the proportion of 2 mol. to 1 mol. iodine (I^2), it is resolved into silver iodide, methyl acetate, hydrogen acetate, carbon dioxide, acetylene, and hydrogen: probably thus:

$$\underset{\text{Silver acetate.}}{2(CH^3.CO^2Ag)} + I^2 = 2AgI + CO^2 + \underset{\text{Methyl acetate.}}{CH^3.CO^2CH^3}$$

$$\underset{\text{Silver acetate.}}{2(CH^3.CO^2Ag)} + I^2 = 2AgI + CO^2 + \underset{\text{Methylene.}}{CH^2} + \underset{\text{Hydrogen acetate.}}{CH^3.CO^2H};\ \text{and}\ 2\underset{\text{Methylene.}}{CH^3} = \underset{\text{Acetylene.}}{C^2H^2} + H^2.$$

In this second reaction, the methyl in one molecule of silver-acetate appears to split up into methylene and hydrogen, the latter taking the place of the silver in another molecule of the acetate, while the methylene is resolved into acetylene and hydrogen.

With *iodine* in presence of *water*, silver acetate yields hydrogen acetate, together with iodide and iodate of silver:

$$6C^2H^3O^2Ag + I^6 + 3H^2O = 6C^2H^4O^2 + 5AgI + AgIO^3.$$

(Birnbaum, *Zeitschr. f. Chem.* [2] v. 452.)

ACETATES (ALCOHOLIC); ACETIC ETHERS.—*a. Monatomic.*—**Amyl Acetate.** $C^5H^{11}.C^2H^3O^2$. The sp. gr. of this ether, according to Mendelejef (*Jahresb.* 1860, p. 7), is 0·8763 at 15° (that of water at 4° being taken as unity). Boiling point 140° (Wanklyn, *Chem. Soc. J.* [2] iii. 30; Schorlemmer, *Jahresb.* 1866, p. 527); 138° (Friedel and Crafts, *ibid.* 1864, p. 460). When heated to 240° with *ethyl-alcohol*, it is partly converted into ethyl acetate. This is the general mode of reaction between alcohols and compound ethers of organic acids, which, in fact, consists in the simple substitution of one alcohol-radicle for another, without formation of water or of acid. (Friedel and Crafts.) Heated in closed vessels in the oil-bath, with *phosphorous chloride*, it yields phosphorous oxide, acetyl chloride, and amyl chloride (Schlagdenhauffen):

$$3(C^5H^{11}.C^2H^3O^2) + 2PCl^3 = P^2O^3 + 3C^2H^3OCl + 3C^5H^{11}Cl.$$

By oxidation with *dilute chromic acid*, it is converted into valeric and acetic acids:

$$C^5H^{11}.C^2H^3O^2 + O^2 = C^5H^{10}O^2 + C^2H^4O^2.$$

(Chapman a. Thorp, *Chem. Soc. J.* [2] lv. 77.) See Ethers.

Cetyl Acetate. $C^{16}H^{33}.C^2H^3O^2$ (i. 840). Sp. gr. 0·858 at 20°. Melting point 18·5°; solidifying point 14°; boiling point 222°—225° (E. Dollfus, *Ann. Ch. Pharm.* cxxxi. 283).

Diallyl Acetates. See Diallyl.

Ethyl Acetate. $C^2H^5.C^2H^3O^2$.—To obtain this ether quite pure, it has been recommended by Engelhardt (*J. Pharm.* [33] xxxix. 159), and more recently by Berthelot (*Ann. Ch. Phys.* [3] lxv. 398), to wash the crude product with a weak alkaline solution; then, after rectification, to agitate it several times with a weak solution of common salt; dry it with pulverulent potassium carbonate (not with calcium chloride, which, being soluble in the ether, gives rise to percussive ebullition in the subsequent rectification); and finally distil at a constant temperature. Frankland and Duppa (*Chem. Soc. J.* [2] iv. 396) prepare acetic ether by gradually pouring a mixture of 3·6 kilogr. of 97 p.c. alcohol and 9 kilogr. strong sulphuric acid on 6 kilogr. sodium acetate previously fused and dried, leaving the mixture to stand for 12 hours, then distilling, and rectifying the distillate (which is free from alcohol and amounts to 6 kilogr.) over fused and pulverised calcium chloride. The best mode of mixing the alcohol and sulphuric acid is to pour the alcohol through a narrow glass tube, and with continual stirring (by means of this tube), to the bottom of the vessel containing the acid; it is advisable also to leave the ethyl-sulphuric acid thus formed for 24 hours, before pouring it upon the sodium acetate.

Sp. gr. 0·8981 at 15° (Mendelejef). Latent heat of liquid, 105·796 heat-units (Favre and Silbermann); of vapour, 154·49 heat-units (Regnault, *Jahresb.* 1863, p. 77). Specific heat of liquid, 0·4344; of vapour referred to constant weight, 0·4008; to constant volume, 1·2184 (Regnault, *Jahresb.* 1863, p. 85).

Reactions.—1. By oxidation with *dilute chromic acid*, it yields nothing but acetic acid: $C^2H^5.C^2H^3O^2 + O^2 = 2C^2H^4O^2$ (Chapman a. Thorp).—2. The action of *chlorine* on this ether has been further examined by Schillerup (*Ann. Ch. Pharm.* cxi. 128). When *chlorine* gas is passed into ethyl acetate in the shade (the liquid being first at the temperature of the air, afterwards heated in the water-bath till it boils) and the passage of the gas being continued till it is no longer absorbed at the latter temperature, a product is obtained which distils without decomposition, but does not yield any compound of constant boiling point by fractional distillation. The portions which distil between 100° and 140° are regarded by Schillerup as mixtures of three chlorinated substitution-products of acetic ether, viz. $C^4H^6Cl^2O^2$, $C^4H^5Cl^3O^2$ and $C^4H^4Cl^4O^2$. On treating these portions with a pasty mixture of barium hydrate and baryta-water, decomposition takes place, and on distilling the product, chloroform and ethyl acetate pass over, leaving a residue of barium chloride and barium formate, mixed with a large quantity of black tarry matter.

3. With *bromine*, acetic ether does not form any substitution-products analogous to those which it yields with chlorine. When 1 molecule of acetic ether is heated to 150° in a close vessel with 2 at. bromine, ethyl bromide and bromacetic acid are produced:

$$C^2H^5.C^2H^3O^2 + Br^2 = C^2H^5Br + C^2H^3BrO^2.$$

Bromacetic acid heated to 180° for three hours with ethyl acetate yields acetic acid and ethyl bromacetate:

$$C^2H^3BrO^2 + C^2H^5.C^2H^3O^2 = C^2H^4O^2 + C^2H^5.C^2H^2BrO^2.$$

(Crafts, *Bull. Soc. Chim.* 1863, p. 117.)

4. Acetic ether distilled with a mixture of lime-water and chloride of lime yields chloroform. (Schlagdenhauffen, *J. Pharm.* [3] xxxvi. 190.)

5. Acetic ether (like compound ethers in general) is decomposed by *anhydrous bases* in the same manner as by the corresponding hydrates, excepting that a metallic derivative of the alcohol (an alcoholate) is formed instead of the alcohol itself; thus:

$$\underset{\text{Ethyl acetate.}}{2(C^2H^5.C^2H^3O^2)} + \underset{\substack{\text{Barium}\\ \text{hydrate.}}}{Ba''H^2O^2} = \underset{\text{Barium acetate.}}{Ba''(C^2H^3O^2)^2} + \underset{\text{Alcohol.}}{2(C^2H^5)HO}$$

$$\underset{\text{Ethyl acetate.}}{2(C^2H^5.C^2H^3O^2)} + \underset{\substack{\text{Barium}\\ \text{oxide.}}}{2Ba''O} = \underset{\text{Barium acetate.}}{Ba''(C^2H^3O^2)^2} + \underset{\text{Barium ethylate.}}{(C^2H^5)^2Ba''O^2}$$

(Berthelot a. Fleurieu, *Ann. Ch. Phys.* [3] xvii. 80.)

6. With *sodium-ethylate*, acetic ether forms a compound decomposible by water,

with formation of alcohol and sodium acetate (Beilstein, *Ann. Ch. Pharm.* cxii. 121):

$$C^2H^5.C^2H^3O^2 + NaC^2H^5O + H^2O = 2C^2H^6O + NaC^2H^3O^2.$$

(See Wanklyn's observations, *infra.*)

7. Ethyl acetate may be heated to 200° with *potassium sulphydrate* without formation of mercaptan (Wanklyn, *Chem. Soc. J.* [2] ii. 418).

Action of the Alkali-metals on Ethyl Acetate.[*]

About thirty years ago this subject was investigated by Löwig and Weidmann, whose paper will be found in the *Journal für praktische Chemie*, Bd. xx. 1840, p. 414 *et seq.* In the same journal there is also an account of the action of potassium on methyl acetate by Weidmann and Schweitzer (*ibid.* p. 386). An analogous result was arrived at in both instances, viz. that the alkali-metal acts on the ether *without evolving any gas*, and gives a solid mass, consisting of ethylate or methylate of the metal, together with a salt of a *reduced acetic acid* (acetylous or hypo-acetylous acid). The equations by which these chemists expressed this reaction are not very intelligible at the present time, but the experimental facts are given with great clearness. A parallel result was obtained with benzoic ether. These researches appear to have been almost forgotten, but they are nevertheless in accordance with the most recent investigations.

A few years ago, Geuther in Germany (*Arch. Pharm.* [2] cxvi. 97; cxxv. 29, 201; *Jahresb.* 1865, p. 304), and Frankland and Duppa in England, experimented on the action of sodium on acetic ether; according to the latter, the action is very complicated (see *Phil. Trans.* 1866, vol. clvi. Part I. p. 37; *Chem. Soc. J.* [2] iv. 396). From the account of this reaction given by Geuther, and the account given by Frankland and Duppa, it would appear that for every equivalent of sodium used up by the ether an equivalent of hydrogen is given off. But the most recent investigations by Wanklyn (*Ann. Ch. Pharm.* 1869, cxlix. 43; cl. 21) have shown that sodium is completely taken up by pure ethyl acetate and by pure amyl acetate, without the slightest evolution of hydrogen, and also that valerianic, butyric, and benzoic ethers do not evolve any gas when they are acted upon by sodium: that, in short, hydrogen is never evolved by the action of the alkali-metals on ethers.[†]

The action of sodium on acetic ether has been shown to be simple, and somewhat analogous to that on the other ethers. It consists in displacement of acetyl by the metal and formation of sodium ethylate and sodium-triacetyl; thus:

$$4Na + 3\left.\begin{matrix}C^2H^3O\\C^2H^5O\end{matrix}\right\} = 3\left.\begin{matrix}Na\\C^2H^5O\end{matrix}\right\} + \left.\begin{matrix}Na\\(C^2H^3O)^3\end{matrix}\right\}.$$

No other direct action takes place between the metal and the ether, it having been shown that just one-fourth of the quantity of metal employed is to be found in the state of sodium-triacetyl subsequently to the termination of the reaction.

A little secondary action, however, takes place between the sodium ethylate and the excess of acetic ether; thus:

$$NaC^2H^5O + \left\{\begin{matrix}C^2H^3O\\C^2H^5O\end{matrix}\right\} = \underset{\text{Ethylene-sodium acetate.}}{NaC^2H^4C^2H^3O^2} + \underset{\text{Alcohol.}}{\left.\begin{matrix}H\\C^2H^5\end{matrix}\right\}O}$$

Of course, the exact conditions under which the experiment is made will determine the extent to which this secondary action proceeds.

The products therefore are:

Direct	Sodium ethylate. Sodium-triacetyl.
Indirect	Ethylene-sodium acetate. Alcohol.

Sodium triacetyl. $C^6H^9NaO^3 = \overset{'''}{Na}(C^2H^3O)^3$.—No doubt the hypoacetylite of soda of the older experimenters was sodium-triacetyl. By Geuther, who first succeeded in obtaining it tolerably pure, and arrived at the true empirical formula $C^6H^9NaO^3$, it was called 'æthylen-dimethylen-carbonsaures-natron,' and was supposed to be derived in a complicated way from acetic ether, its formation being accompanied by the evolution of a quantity of hydrogen equivalent to the sodium reacting on the ether. Frankland and Duppa, whose account of its origin involves the same supposition, termed it 'Ethylic sodacetone-carbonate.'

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[*] Communicated by Professor Wanklyn.

[†] Since the above was written, the non-evolution of hydrogen has been confirmed by Ladenburg (*Deut. Chem. Gesellsch. Ber.* 1870).

Preparation.—The slightly yellow wax-like mass, resulting from the action of sodium on acetic ether (1 part of sodium to 8 parts of acetic ether should be taken, and the materials heated in the water-bath, or even a little higher, until the metal has disappeared), is dissolved in perfectly dry ether mixed with a little absolute alcohol, the solution filtered or decanted, and the filtrate set aside to crystallise. Crystals of sodium-triacetyl separate. This compound is soluble in water, and apparently cannot be recovered from its aqueous solution. By treatment with an equivalent of acetic acid and common ether, it is resolved into the corresponding hydrogen compound, viz. $H(C^2H^3O)^3$, hydrogen-triacetyl, which is an oil, rather heavier than water (sp. gr. at 5° = 1·03), and boils at 181°. It was called 'Æthyldiacetsaure' by its discoverer Geuther. It shows an acid reaction with litmus only in presence of water. With neutral ferric chloride it gives a characteristic dark violet-red colour. It may be distilled unchanged in contact with steam, but undergoes decomposition in presence of strong acids or alkalis, or even in contact with water alone at a temperature of 150°. A number of its metallic derivatives have been obtained. The decomposition effected by water in presence of acids or alkalis is very interesting, viz.,

$$C^6H^{10}O^3 + H^2O = \underset{\text{Acetone.}}{C^3H^6O} + \underset{\text{Alcohol.}}{C^2H^6O} + CO^2;$$

wherein, as will be seen, alcohol is produced by a substance derived from acetic acid, inasmuch as the triacetyl is derived solely from the acetyl present in acetic ether.

Hydrogen triacetyl has also been obtained by Lippmann (*Zeitschr. f. Chem.* [2] v. 28)—who, however, calls it *ethylic acetone carbonate*—by the action of acetyl chloride on the product of the action of sodium on acetic ether (doubtless on the ethylene-sodium acetate contained therein):

$$NaC^2H^4C^2H^3O^2 + C^2H^3OCl = NaCl + C^6H^{10}O^3.$$

He finds that it is violently attacked by sodium, with evolution of hydrogen and formation of sodium-triacetyl; and that this compound heated with a solution of mercuric chloride in acetic ether yields a precipitate of *mercuric triacetyl*, $C^6H^8Hg''O^3$. Both hydrogen-triacetyl and mercuric triacetyl unite directly with *bromine*, forming the compounds $C^6H^{10}O^3Br^2$ and $C^6H^8HgO^3Br^2$, both of which are heavy, pungent, oily liquids.

Noeldecke (*ibid.* iv. 681), by treating the product of the action of sodium on ethyl-acetate with ethyl-chloracetate, has obtained an acid, $C^5H^8O^3$, homologous with $C^6H^{10}O^3$, together with succinic acid. The ethylic ethers of the two acids resulting from the reaction were converted into sodium salts by treatment with caustic soda, and these salts were separated by absolute alcohol, which dissolved the salt $C^5H^7NaO^3$, leaving the succinate undissolved. The formation of ethyl-succinate is represented by the equation:

$$NaC^2H^4C^2H^3O^2 + C^2H^5.C^2H^2ClO^2 = NaCl + (C^2H^5)^2.C^4H^4O^4.$$

For the equations representing the formation of the ethylic ether of the acid $C^5H^8O^3$, regarded by Noeldecke as acetyl-propionic acid, $C^3H^5(C^2H^3O)O^2$, we must refer to his memoir. This acid is monobasic, and forms crystallisable salts with calcium, copper, and zinc.

Ethylic and *methylic derivatives* have been obtained by the action of iodide of ethyl or methyl on sodium-triacetyl. Both of them were first described by Geuther, and the ethylic compound has also been specially examined by Frankland and Duppa.

Ethyl-triacetyl, $C^2H^5(C^2H^3O)^3$, boils at 198°; sp. gr. at 12° = 0·998 (Geuther). Frankland and Duppa give the boiling point 195°, and the sp. gr. at 16·6° = 0·9834.

Methyl-triacetyl, $CH^3(C^2H^3O)^3$, boils at 187°; sp. gr. at 6° = 1·009 (Geuther).

Just as hydrogen-triacetyl yields acetone, alcohol, and water, by the action of alkalis upon it, so also do these derivatives, ethyl- and methyl-triacetyl, suffer an analogous decomposition. Thus ethyl-triacetyl, under the influence of alkalis, as when boiled with potash, or when treated with baryta-water, yields a ketone $C^5H^{10}O$, together with alcohol:

$$C^2H^5(C^2H^3O)^3 + H^2O = C^5H^{10}O + C^2H^6O + CO^2.$$

In addition to sodium-triacetyl, produced by the direct action of sodium on acetic ether, it has been explained that another new organic product, viz.,

Ethylene-sodium acetate, is produced by a secondary action of acetic ether on some of the sodium-ethylate, resulting as the complement to the sodium-triacetyl.

When, therefore, the crude mass, obtained by the prolonged action of acetic ether on sodium, is treated with ethyl-iodide, the following products will be formed:

From sodium-ethylate	common ethylic ether.
From sodium-triacetyl	ethyl-triacetyl.
From ethylene-sodium acetate . . .	$C^{10}H^{18}O^3$ (new body).

The formation of the new body $C^{10}H^{18}O^3$, which was obtained by Frankland and Duppa, and named 'ethylic-diethacetone-carbionate,' is explained by its discoverers on the assumption that hydrogen is evolved during the reaction. Unpublished researches by Wanklyn have shown, however, that ethylene-sodium acetate prepared by the action of acetic ether on sodium ethylate yields the oily liquid $C^{10}H^{18}O^3$, thus:

$$\underset{\text{Ethylene-sodium acetate.}}{2Na\left\{\begin{matrix}C^2H^4\\O^2C^2H^3\end{matrix}\right.} + 2C^2H^5I = Na^2I^2 + \underset{\text{Alcohol.}}{C^2H^6O} + \underset{\text{New body.}}{C^{10}H^{18}O^3}$$

The new body $C^{10}H^{18}O^3$ boils at 210° to 212° without decomposition; sp. gr. at 20° = 0·9738. It possesses the property of being resolved by baryta or lime-water into carbon dioxide, alcohol, and a ketone, thus:

$$C^{10}H^{18}O^3 + H^2O = CO^2 + C^2H^6O + C^7H^{14}O.$$

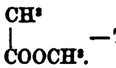
It has thus been stated that, by the action of ethyl iodide on the crude wax-like product of the action of sodium on acetic ether, there is produced ethyl-triacetyl, $C^8H^{14}O^3$, and a new body, $C^{10}H^{18}O^3$. Now both of these oily products have high boiling points, and are capable of reacting on the undecomposed sodium ethylate produced by the direct action of sodium on acetic ether. By this reaction it has recently been shown by Geuther that butyric ether is produced. Geuther made ethyl-triacetyl, and then exposed sodium ethylate to its action, and obtained a very large quantity of butyric ether thus:

$$C^8H^{14}O^3 + NaC^2H^5O = \underset{\text{Ethylene-sodium acetate.}}{NaC^2H^4C^2H^3O^2} + \underset{\text{Ethyl butyrate.}}{C^6H^{12}O^2}$$

By a similar reaction no doubt $C^{10}H^{18}O^3$ will be found to give rise to caproic ether, thus:

$$C^{10}H^{18}O^3 + NaC^2H^5O = \underset{\text{Ethylene-sodium acetate.}}{NaC^2H^4C^2H^3O^2} + \underset{\text{Ethyl caproate.}}{C^8H^{16}O^2}$$

Such is, then, the true chemical history of the butyric ether (and probably of the caproic ether) obtained by Frankland and Duppa by the successive action of sodium and ethyl-iodide on acetic ether. The butyric ether is a product of ethyl-triacetyl and sodium-ethylate. Frankland and Duppa explained the production of both butyric and caproic ether, by assuming the evolution of hydrogen gas, and the production of the so-called sod-acetic ether and disod-acetic ether, which, by action of ethyl-iodide, were supposed to give butyric and caproic ether respectively. J. A. W.

Methyl Acetate. $C^3H^6O^2 = \left.\begin{matrix}C^2H^3O\\CH^3\end{matrix}\right\}O =$  $\begin{matrix}CH^3\\ \vert\\ COOCH^3.\end{matrix}$ —This ether is resolved by oxidation with *dilute chromic acid* into acetic acid, carbon dioxide and water: $C^3H^6O^2 + O^3 = C^2H^4O^2 + CO^2 + H^2O$ (Chapman and Thorp). The action of *sodium* upon it is analogous to that which the same metal exerts upon ethyl acetate (p. 15), the direct products being sodium-methylate and sodium-triacetyl.

Methyl acetate subjected to the action of *chlorine* under various circumstances yields the four chlorinated derivatives, $C^3H^5ClO^2$, $C^3H^4Cl^2O^2$, $C^3HCl^5O^2$ and $C^3Cl^6O^2$. The first, third and fourth are described in vol. i. pp. 23, 24.

Pentachlorinated methyl acetate, $C^3HCl^5O^2$, is formed by the action of chlorine on alkaline citrates, and is also the final product of the action of chlorine on methyl acetate in the shade. It is converted by caustic alkalis into dichloracetate, chloride and carbonate:

$$\left.\begin{matrix}C^2HCl^2O\\CCl^3\end{matrix}\right\}O + 6KHO = \left.\begin{matrix}C^2HCl^2O\\K\end{matrix}\right\}O + 3KCl + CK^2O^3 + 3H^2O.$$

Aqueous *ammonia* yields similar products; with alcoholic ammonia, dichloracetamide, $C^2H^3Cl^2NO$, is produced, instead of ammonium dichloracetate (Cloez, *Ann. Ch. Phys.* [3] xvii. 297, 311; *Jahresb.* 1861, p. 369).

Pentabrominated methyl acetate, $C^3HBr^5O^2$, is produced by the action of bromine on the citrates of potassium, sodium and barium. Cahours, who obtained it in this manner, together with bromoform, designated it as bromoxaform (see CITRIC ACID, i. 906); Cloez (*Rép. Chim. pure*, 1862, p. 127) obtains it also by the action of bromine on methylic alcohol or methyl acetate. It is a solid body, insoluble in water, soluble in alcohol, which deposits it by spontaneous evaporation in beautiful plates, melting at 75°, decomposed by distillation, and transformed by hot concentrated potash-solution into potassium bromide, bromoform and potassium oxalate (Cahours, i. 707). According to Cloez, aqueous potash and ammonia decompose it, with formation of carbonate and formate, whereas with alcoholic ammonia it yields dibromacetamide.

Phenyl Acetate. $C^6H^5.C^2H^3O^2$.—This compound, discovered by Scrugham (i. 24), may be prepared in the pure state by heating 20 pts. of dehydrated lead acetate, 3 pts. of phenol, and an excess of carbon bisulphide to 170°, in sealed tubes, which must be opened from time to time, to prevent explosion. The portion of the product which boils above 190° yields phenyl acetate by fractional distillation, as a colourless liquid, having a peculiarly pungent odour, a sp. gr. of 1·074, vapour-density, obs. = 4·727, calc. 459, and boiling at 200°. It becomes yellowish by keeping, dissolves in water, reacts neutral, and is scarcely decomposed by water even at 180°. Boiled with potash-ley it yields phenol and potassium acetate. It has the same index of refraction as easily fusible German glass, inasmuch as tubes of this glass become invisible when immersed in it (J. Broughton, *Chem. Soc. J.* [2] iii. 21). Heated with an equal weight of *aniline* in a flask with upright condensing tube, or in a sealed tube to 250°, it yields phenol and acetanilide (Lauth, *Bull. Soc. Chim.* [2] ii. 164).

$$\left.\begin{matrix}C^2H^3O\\C^6H^5\end{matrix}\right\}O + \left.\begin{matrix}C^6H^5\\H^2\end{matrix}\right\}N = \left.\begin{matrix}C^6H^5\\H\end{matrix}\right\}O + \left.\begin{matrix}C^6H^5\\C^2H^3O\\H\end{matrix}\right\}N.$$

Acetates of Diatomic Alcohol-radicles: Amylene, Butylene, Ethylene, &c.—The recent additions to the chemical history of these ethers will be given in connection with the respective diatomic alcohols.

SUBSTITUTION-DERIVATIVES OF ACETIC ACID.

Bromacetic Acid, $C^2H^3BrO^2$, described at p. 664, vol. i., as formed by the action of bromine on acetic acid, is likewise produced: *α*. Together with dibromhydrin and other products, by the action of bromine on anhydrous glycerin (L. Barth, *Ann. Ch. Pharm.* cxxiv. 341).—*β*. Together with ethylic bromide, by the action of bromine on ethylic acetate: in sealed tubes at 150°:

$$C^2H^5.C^2H^3O^2 + Br^2 = C^2H^3BrO^2 + C^2H^5Br.$$

Part of the bromacetic acid is further converted into dibromacetic acid (Crofts, *ibid.* cxxix. 50).—*γ*. By the action of hydrobromic acid on glycollic acid: $C^2H^4O^3 + HBr = H^2O + C^2H^3BrO^2$ (Kekulé, *ibid.* cxxx. 11).—*δ*. By oxidation of an alcoholic solution of monobromacetylene exposed to the air: $C^2HBr + O + H^2O = C^2H^3BrO^2$ (Glöckner, *Ann. Ch. Pharm. Suppl.* vii. 107).

This acid acts on *silver benzoate* in such a manner as to form glycollide, benzoic acid and silver bromide:

$$C^2H^3BrO^2 + AgC^7H^5O^2 = C^2H^2O^2 + C^7H^6O^2 + AgBr.$$

With *sodium salicylate*, it forms glycollide and salicylic acid.

The *lead-salt*, $Pb''(C^2H^2BrO^2)^2$, crystallises, according to A. Naumann (*Jahresb.* 1864, p. 322), not in needles, as stated by Perkin and Duppa, but in white shining laminæ, and is decomposed by prolonged boiling of its aqueous solution into bromide and glycollate of lead. The sodium salt is decomposed in a similar manner.

The ethylic ether heated with sodium is converted, as already observed (p. 2), into the ethylic ethers of aceconitic acid and citracetic acid.

Tribromacetic Acid, $C^2HBr^3O^2$, is produced by the action of water on tribromacetic bromide (p. 21). It forms crystals which melt at 135°, boil at 250°, and yield with potash decomposition-products analogous to those obtained from trichloracetic acid; namely, a salt of formic acid and bromoform.

Chloracetic Acid, $C^2H^3ClO^2$, and **Dichloracetic Acid,** $C^2H^2Cl^2O^2$, may be advantageously prepared by treating boiling acetic acid (diluted to sp. gr. 1·065) with chlorine in presence of iodine. Half a litre of the acid is heated to boiling with 40 to 60 grams of iodine in a flask-retort, having a long upright neck, and dry chlorine gas is passed in a moderate stream through a tube dipping into the liquid; a side tube serves for the escape of hydrochloric acid gas, while the vapours condensed in the long neck flow back again into the flask. The chlorine begins to act strongly only when the iodine is converted into perchloride; if the current of chlorine is too slow, free iodine sublimes; but on accelerating the stream of chlorine, this iodine flows back in the form of monochloride, which is subsequently converted into trichloride, and then acts upon the acetic acid. After the passage of the chlorine has been continued for several days, the liquid is boiled till vapours of iodine make their appearance, then left to cool, and the decanted liquid is distilled. The portion boiling below 180° (which contains the unaltered acetic acid and the greater part of the iodine) is again subjected to the action of chlorine. The distillate which passes over crystallises on cooling, and yields by repeated distillation and crystallisation, pure monochloracetic acid. The iodine-vapours given off during the distillations arise from a small quantity of iodacetic acid, which is always produced in a certain quantity, but may be removed by repeated distillation or by treatment with a small quantity of concentrated hydriodic acid. The portion of the product boiling above 188° (which does not amount to so much as the monochlorinated acid, except in favourable cases, and after at least sixty hours' action of the chlorine), consists chiefly of dichloracetic acid, which must be freed from a little iodacetic acid in the manner above described, and then purified by fractional distillation. Lastly, the portion of the crude distillate boiling between 195° and 210°, appears to contain trichloracetic acid (Hugo Müller, *Chem. Soc. J.* [2] ii. 398).

Monochloracetic acid, $C^2H^3ClO^2$, is described at p. 875, vol. i., together with several of its salts. The *sodium salt*, prepared by saturating the aqueous acid in the cold with sodium carbonate, does not yield any distinct crystals by evaporation in a vacuum. A specimen dried in this way remained unaltered when heated to a little below 100°; above that temperature it melted, turned brown and swelled up (Heintz, *Jahresb.* 1861, p. 444).

Ethyl chloracetate, $C^2H^5.C^2H^2ClO^2$, is easily prepared by passing hydrochloric acid gas into an alcoholic solution of the acid, and precipitating with water. Heated to 130°–150°, with rather more than an equivalent quantity of sodium glycollate, it is converted into ethyl glycollate, $C^2H^5.C^2H^3O^3$ (Heintz).

Dichloracetic acid, $C^2H^2Cl^2O^2$ or $H.C^2HCl^2O^2$, may be prepared as above, or, according to Maumené (*Bull. Soc. Chim.* [2] i. 417), by leaving 5 at. dry chlorine to act upon 3 molecules of pure monochloracetic acid, in large flasks, for twenty-four hours. By heating the very corrosive product in the water-bath to remove hydrochloric acid, and then distilling it, without the use of corks, pure dichloracetic acid is obtained as the last portion of the distillate.

Dichloracetic acid is, at ordinary temperatures, a liquid of sp. gr. 1·526 at 15°, boiling at 195°, very corrosive, and emitting suffocating vapours when heated. According to H. Müller, it does not solidify in the cold; according to Maumené, it crystallises in distorted rhombohedral plates. It appears to be easily decomposed by water, with formation of hydrochloric acid (Müller). Its salts are mostly soluble in water; those of the alkali metals crystallise with difficulty. The *lead-salt* is amorphous, soluble in water, but insoluble in alcohol. The *silver-salt*, $AgC^2HCl^2O^2$, crystallises indistinctly, and decomposes in aqueous solution, with separation of silver chloride and metallic silver (Müller). According to Maumené, it is obtained by digesting the acid with silver oxide suspended in water at 40°, as a sparingly soluble crystalline precipitate, which, when warmed, is very easily resolved, like the trichloracetate, into monochloracetic and hydrochloric acids, together with carbon dioxide, carbon monoxide. water and silver chloride. The solution, heated to 75°–80° with silver oxide, is decomposed in the manner shown by the equation:

$$2AgC^2HCl^2O^2 + 3Ag^2O = 2CO^2 + 2CO + 4AgCl + Ag^4 + H^2O.$$

Ethyl dichloracetate, $C^2H^5.C^2HClO^2$, is formed, together with other products, by heating carbon dichloride C^2Cl^4 with sodium ethylate to 100°–150° for twelve or eighteen hours. The portion of the product which is soluble in water consists of sodium ethyl-glyoxylate. (See GLYOXYLATES.) The oily portion separable by water consists mainly of ethyl dichloracetate (with a small quantity of dichloracetic chloride, p. 22). This ether has a density of 1·29, and boils at 153° (at 156°, Müller). Heated with water to 120°, it is resolved into glyoxylic acid, $C^2H^4O^4$, hydrochloric acid and alcohol; on keeping it, oxalic acid is produced, together with alcohol (Fischer and Geuther, *Jahresb.* 1864, p. 316). The *methylic ether* exhibits similar properties, and has a sweet taste and aromatic odour (Müller).

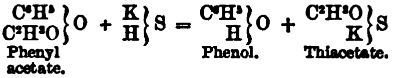
Cyanacetic Acid, $C^2H^3(CN)O^2$, or its ethylic ether, is produced by boiling ethylmonochloracetate with aqueous potassium cyanide. The ether treated with strong potash-ley gives off ammonia, and is converted into malonic acid, $C^3H^4O^4$ (Kolbe, *Ann. Ch. Pharm.* cxxxi. 221; H. Müller, *ibid.* cxxxi. 350).

Th. Meves (*Ann. Ch. Pharm.* cxliiii. 201) prepares cyanacetic acid by heating 250 grms. ethyl monochloracetate with a solution of 300 grms. potassium cyanide in 1,200 grms. water in an oil-bath till the odour of prussic acid is no longer perceptible, evaporating the exactly neutralised dark brown liquid to half its bulk, acidulating the filtered liquid with sulphuric acid, evaporating, and repeatedly treating the residue with ether. The united ethereal solutions when evaporated leave the crude cyanacetic acid as a dark brown liquid, which must be treated with lead carbonate (to remove malonic acid), filtered, and, after precipitation of the lead by hydrogen sulphide, evaporated first over the water-bath, then in a vacuum over sulphuric acid. The crystallised and only slightly coloured cyanacetic acid thus obtained forms salts which, excepting those of silver and mercury, are very soluble in water:

Potassium cyanacetate, $C^2H^2(CN)O^2K$, is deliquescent.
Silver „ $C^2H^2(CN)O^2Ag$, sulphur-yellow precipitate.
Barium „ $[C^2H^2(CN)O^2]^2Ba$, does not crystallise well.
Copper „ $[C^2H^2(CN)O^2]^2Cu$, green needles.
Lead „ $[C^2H^2(CN)O^2]^2Pb.H^2O$, spicular crystals.
Mercuric „ $[C^2H^2(CN)O^2]^2Hg.2HgO$, white powder.
Zinc „ $[C^2H^2(CN)O^2]^2Zn.2H^2O$, indistinctly crystalline.

Iodacetic Acid. $C^2H^3IO^2$.—*Preparation and Properties* (iii. 279). Resolved by concentrated hydriodic acid, even in the cold, into acetic acid and free iodine: $C^2H^3IO^2 + HI = C^2H^4O^2 + I^2$ (Kekulé, *Chem. Soc. J.* [2] ii. 365).

Thiacetic Acid. $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}S$ (v. 771).—Formed by the action of potassium sulphydrate in alcoholic solution on phenyl acetate.



$$\left.\begin{matrix}C^6H^5\\C^2H^3O\end{matrix}\right\}O + \left.\begin{matrix}K\\H\end{matrix}\right\}S = \left.\begin{matrix}C^6H^5\\H\end{matrix}\right\}O + \left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}S$$

Phenyl acetate. Phenol. Thiacetate.

On adding water, the phenol separates and the potassium thiacetate dissolves (Kekulé, *Zeitschr. f. Chem.* [2] iii. 196). According to Fröhde (*Jahresb.* 1866, p. 157), sodium thiacetate is formed by heating lead acetate with sodium hyposulphite.

Ethyl thiacetate, $C^2H^3OS.C^2H^5$, may be prepared by dropping acetyl chloride on sodium mercaptide, the reaction being assisted towards the end by the application of a gentle heat. It is a colourless liquid, having an alliaceous odour, and boiling at 117°. When dropped into cooled nitric acid of sp. gr. 1·2, diluted with an equal bulk of water, it is oxidised to sulphethylic acid (Saytzeff, *Zeitschr. f. Chem.* [2] iv. 642).

Thiacetic Anhydride, or *Acetic Sulphide*, $(C^2H^3O)^2S$, may be prepared by adding acetyl chloride by small portions to crystallised potassium sulphide contained in a well-cooled flask, provided with a condenser. On distilling the liquid at the end of the reaction, pure thiacetic anhydride passes over, as a yellowish liquid boiling at 121°. It is not attacked by dilute nitric acid, but fuming nitric acid oxidises it to acetic and sulphuric acids. Not decomposed by heating with acetyl iodide or ethyl iodide (Saytzeff).

ACETIC BROMIDE, or **ACETYL BROMIDE.** $C^2H^3O.Br$.—H. Gal (*Bull. Soc. Chim.* v. 172) prepares this compound by introducing 6 at. bromine through a drawn-out tube into a retort containing 3 mols. of glacial acetic acid, and 2 at. red phosphorus. A violent reaction then takes place, resulting in the formation of hydrobromic acid, phosphorous acid, and acetic bromide, which is separated by distillation:

$$3C^2H^4O^2 + 2PBr^3 = 3HBr + P^2O^3 + 3C^2H^3OBr.$$

According to this equation, half the bromine is employed in the formation of the acetic bromide, whereas according to the ordinary method with phosphorus pentabromide (i. 34) only $\frac{1}{5}$th of the bromine is converted into that compound; 240 grms. bromine, 90 grms. glacial acetic acid, and 33 grms. phosphorus, yield 140 grms. acetic bromide boiling at 81°.

Monobromacetic Bromide. $C^2H^2BrO.Br$.—Produced: 1. By heating 6 grms. acetic bromide with 8 grms. bromine in sealed tubes placed in a water-bath heated to 50° or 60° (the tubes being opened from time to time to allow of the escape of hydrobromic acid); by collecting the portion of the product which distils over at 151°–153°, it is obtained as a yellowish liquid, which may be rendered colourless by agitation with mercury.—2. By heating acetic bromide with an equivalent quantity of phosphorus pentabromide to 140°–150° in a sealed tube:—$C^2H^3OBr + PBr^5 = PBr^3 + HBr + C^2H^2BrO.Br$ (Samosadsky, *Zeitschr. f. Chem.* [2] vi. 105).—

3. Hübner (*Ann. Ch. Pharm.* cxxiv. 315) and Naumann (*ibid.* cxxix. 257) prepare it by the action of bromine on acetic chloride. When these substances are heated together in equivalent proportions (120 pts. bromine to 64 pts. acetic chloride) to 100° in a retort connected with an upright condensing tube, the reaction takes place chiefly in the manner represented by the equation $C^2H^3OCl + Br^2 = C^2H^2BrO.Br + HCl$. By repeatedly rectifying the red liquid which remains in the retort, and collecting the portion which boils above 148°, the monobromacetic bromide is obtained as a colourless or light yellow liquid boiling at 149°–150°. It fumes in the air, strongly attacks the mucous membranes of the nose and bronchial tubes, and produces deep wounds when placed upon the skin; its vapour instantly destroys cork and caoutchouc. It is not decomposed by sodium even with aid of heat. It mixes in all proportions with anhydrous *ether* (Naumann, Hübner). It dissolves slowly in *water*, forming hydrobromic and bromacetic acids, the latter of which may be obtained in fine crystals by leaving the bromide exposed to the acid. With *alcohol* it yields ethyl bromide and ethylic monobromacetate boiling at 159°. By heating with *bromine*, it is converted into dibromacetic bromide (Gal). Neutralised with *sodium carbonate*, and evaporated, it leaves a saline mass, containing a small quantity of sodium bromacetate, together with sodium bromide and glycollic acid. Distilled with an equivalent quantity of dry *sodium acetate*, it yields up to 100° chiefly acetic oxide, $(C^2H^3O)^2O$; between 178° and 195°, bromacetic oxide, $(C^2H^2BrO)^2O$; and above 200° bromacetic acid, as a decomposition-product of the latter. With 1 mol. bromacetic bromide and 2 mols. sodium acetate (equal weights), the reaction takes place as shown by the equation:

$$\underset{\text{Bromacetic bromide.}}{C^2H^2BrO.Br} + \underset{\text{Sodium acetate.}}{2NaC^2H^3O^2} = \underset{\text{Glycollide.}}{C^2H^2O^2} + \underset{\text{Acetic oxide.}}{C^4H^6O^3} + 2NaBr \text{ (Naumann).}$$

Dibromacetic Bromide, $C^2HBr^2O.Br$, is formed by heating 1 mol. monobromacetic bromide with 2 at. bromine to 150° for several days, and distilling the contents of the tube. It is colourless, fumes in the air, boils at 194°, dissolves slowly in water, yields no crystals on exposure to the air, is easily decomposed by potash, and when treated with alcohol yields ethylic dibromacetate, $C^2H^5.C^2HBr^2O^2$, boiling at 194° (?) (Gal, *loc. cit.*).

Tribromacetic Bromide, $C^2Br^3O.Br$, is produced by heating dibromacetic bromide with excess of bromine to 200°, as long as hydrobromic acid continues to be evolved, and may be obtained pure by distillation, between 220° and 225°. It is a liquid which fumes in the air, and is converted by prolonged contact with *water* into tribromacetic acid; by *alcohol* into ethylic tribromacetate, $C^2H^5.C^2Br^3O^2$, boiling at 225° (Gal).

Chloracetic Bromide. $C^2H^2ClO.Br$ or $CH^2Cl.COBr$ (P. de Wilde, *Ann. Ch. Pharm.* cxxx. 372; *Jahresb.* 1864, p. 320; Gal, *loc. cit.*).—Prepared by adding 6 at. bromine, by drops, or in a thin stream, to a mixture of 3 at. monochloracetic acid, and 2 at. amorphous phosphorus:

$$3(C^2H^2ClO.H.O) + 2PBr^3 = 3HBr + P^2O^3 + 3(C^2H^2ClO.Br).$$

By distillation, the chloracetic bromide is obtained as a colourless liquid, turning red or yellow after a few days, fuming in the air, and exciting lacrymation. Sp. gr. 1·913 at 9°; B. P. 127° (De Wilde); 133° to 135° (Gal). In contact with water it yields hydrobromic and monochloracetic acids, and with alcohol, ethylic bromide and ethylic monochloracetate.

Cyanacetic Bromide, $C^2H^2(CN)O.Br$ or $CH^2Cy.COBr$, is produced, together with its isomer, bromacetic cyanide, $C^2H^2BrO.CN$, by heating silver cyanide for an hour in the water-bath, with a mixture of bromacetic bromide and chloroform. The liquid extracted by hot ether from the resulting silver bromide deposits, first, long, very sparingly soluble needles of cyanacetic bromide, and some time afterwards large transparent plates of bromacetic cyanide. The sparingly soluble cyanacetic bromide crystallises from boiling chloroform or ether in needles, but from a mixture of chloroform and glacial acetic acid in small cubes. When decomposed by water or potash it does not yield hydrocyanic acid, but, together with ammonium bromide (or ammonia and potassium bromide), the acids which result from the mutual action of ethylic chloracetate and potassium cyanide, viz. cyanacetic and malonic acids (p. 19) (Hübner, *Jahresb.* 1862, p. 243; 1864, p. 323).

ACETIC CHLORIDE, or **ACETYL CHLORIDE.** $C^2H^3O.Cl$ or $CH^3.COCl$ (i. 35).—This compound is contained in the more volatile portion of the product obtained by the action of chlorine on anhydrous aldehyde. By the further action of *chlorine* it is converted into monochloracetic chloride (Wurtz, *Ann. Ch. Phys.* [3] xlix. 58).

With *potassium sulphydrate*, it yields acetic sulphydrate or thiacetic acid (v. 771), and with *potassium monosulphide*, it yields acetic sulphide or thiacetic anhydride:

$$C^2H^3OCl + KHS = KCl + C^2H^3O.HS$$

and

$$2C^2H^3OCl + K^2S = 2KCl + (C^2H^3O)^2S$$

(Jacquemin a. Vosselmann, *Compt. rend.* xlix. 371). With *zinc-methyl*, it forms acetone or dimethyl ketone:

$$2C^2H^3OCl + Zn(CH^3)^2 = ZnCl^2 + CO(CH^3)^2;$$

and with *zinc-ethyl*, in like manner, the homologous compound methyl-ethyl ketone, $CO(CH^3)(C^2H^5)$, isomeric with butyrone (Freund, *Ann. Ch. Pharm.* cxviii. 1). Heated in a sealed tube with *phosphorus pentachloride*, it yields trichloracetic chloride, $C^2Cl^3O.Cl$, a small quantity of an oily compound, C^2H^3Cl,, which distil over successively (the latter depositing crystals in the receiver), and a crystalline compound, C^2HCl^5, which remains in the retort and melts at 180°–181° (Hübner, *Ann. Ch. Pharm.* cxx. 330). By *silver cyanide*, acetic chloride is converted into acetic cyanide, $C^2H^3O.CN$ (Hübner). Acetic chloride acts violently on lime which has been slaked and then ignited, the lime sometimes becoming red-hot. On lead oxide, on the contrary, it acts but slightly, even at 100°–150°. When 2 mols. acetic chloride are gently heated in a sealed tube with 1 mol. caustic baryta, and the product distilled, acetic oxide passes over (H. Gal, *Jahresb.* 1863, p. 321). Heated to 120° with *phosphorous acid*, it yields, as principal product, acetopyrophosphorous acid, $H^3P(C^2H^3O)O^3$ (Menschutkin, iv. 534).

Monobromacetic Chloride, $C^2H^2BrO.Cl$, is produced by the action of phosphorus trichloride on monobromacetic acid:

$$3C^2H^3BrO^2 + PCl^3 = PH^3O^3 + 3(C^2H^2BrO.Cl).$$

It is a colourless, slightly fuming liquid, having a pungent odour, and a sp. gr. of 1·908 at 9°. By the slow access of aqueous vapour, it is converted into monochloracetic acid (B. P. 180°) and monobromacetic acid (B. P. 208°) (Geuther, *Ann. Ch. Pharm.* cxxxii. 171).

Monochloracetic Chloride. $C^2H^2ClO.Cl$.—Produced: 1. By the action of dry chlorine gas on acetic chloride, rapidly in sunshine, in the course of 24 hours in diffused daylight; separated by fractional distillation (Wurtz, *Ann. Ch. Pharm.* cii. 93).—2. By the action of phosphorus trichloride on monochloracetic acid (De Wilde, Gal).—3. By that of phosphorus pentachloride on sulphacetylenic chloride (v. 476).

$$\left.\begin{matrix}SO^2\\C^2H^2\end{matrix}\right\}\begin{matrix}O\\Cl^2\end{matrix} + PCl^5 = SO^2Cl^2 + C^2H^2ClO.Cl + PCl^3.$$

It is a colourless liquid, having a pungent odour, sp. gr. 1·495 at 0°, and boiling at about 105° (Wurtz). Converted by *water* into chloracetic acid; by *alcohol* into ethyl chloracetate; by dry *ammonia* gas into chloracetamide, $C^2H^2ClO.NH^2$.

Dichloracetic Chloride, $C^2HCl^2O.Cl$, has not been obtained, but its ethylic derivative, $C^2(C^2H^5)Cl^2O.Cl$, is formed, together with ethyl dichloracetate and other products, by the action of sodium ethylate on carbon dichloride, C^2Cl^4. If the portion of the product of this reaction which boils at 153° be shaken up with excess of potash-ley, the ethyl dichloracetate dissolves, with formation of chloride, oxalate and dichloracetate of potassium, while the dichlorethylacetic chloride remains undissolved. It is a liquid having a peculiar acrid ethereal odour, boiling at 152°–153°; remains unaltered in dry air, or in contact with potash, ammonia, or water, but is easily decomposed by moist air, with formation of oxalic and hydrochloric acids. When heated with *water* it gradually dissolves, yielding alcohol, hydrochloric and glyoxylic acids, with traces of oxalic acid:

$$C^2(C^2H^5)Cl^2O.Cl + 4H^2O = C^2H^6O + 3HCl + C^2H^4O^4$$

(Geuther, *Jahresb.* 1864, p. 317).

Trichloracetic Chloride, $C^2Cl^3O.Cl$, is formed, together with tri- and pentachlorinated ethane, $C^2H^3Cl^3$ and C^2HCl^5, by the action of phosphorus pentachloride on acetic chloride. It is a liquid boiling at 118° (Hübner, *Jahresb.* 1861, p. 437).

ACETIC CYANIDE or **ACETYL CYANIDE.** $C^3H^3ON = C^2H^3O.CN$.—Produced by the action of acetic chloride on silver cyanide. On heating the two compounds together to 100° in a sealed tube for an hour or two, and subsequently distilling the product, a colourless liquid distils over between 80° and 90°, and afterwards a compound which boils at a much higher temperature. The first-mentioned liquid yields by repeated rectification, acetic cyanide, which boils constantly at 93°, and has a vapour-density of 2·4, agreeing with the formula $C^2H^3O.CN$ for a two-volume condensation (calc. 2·3). This compound is lighter than water, which gradually dissolves it, with formation of hydocyanic and acetic acids; it smells of these acids, and by prolonged contact with the air is converted into crystals soluble in water. When kept in a vessel closed with a cork, or heated with solid potassium hydrate or with sodium, it changes into an oil insoluble in water, and solidifying when washed with water to crystals, which have the composition of acetic cyanide, but a vapour-density of 4·9 to 5·0, agreeing with the formula of diacetic dicyanide, $(C^2H^3O)^2.(CN)^2$ (calc. 477). This compound melts at 69° and boils at 208°–209°. When gently heated it remains liquid for a long time, and gradually solidifies again in very large plates. It dissolves in alcohol, ether, ordinary sulphuric acid, strong acetic acid, and strong ammonia, gives off ammonia when boiled with potash, and, like the liquid cyanide, is converted into hydrocyanic and acetic acids by boiling with water, sulphuric acid, or potash. Heated in a sealed tube to 100° with solution of silver nitrate, it yields silver cyanide crystallising in shining needles (H. Hübner, *Ann. Ch. Pharm.* cxx. 230; cxxiii. 271).

Bromacetic Cyanide, $C^2H^2BrO.CN$, is obtained, together with its isomer, cyanacetic bromide, by heating silver cyanide with bromacetic bromide and chloroform (p. 21).

ACETIC OXIDE or **ANHYDRIDE.** $(C^2H^3O)^2O$.—The following additional modes of preparing this compound may be noticed: *a*. By the action of caustic baryta on acetic chloride, C^2H^3OCl, in sealed tubes, first at ordinary temperatures, afterwards at a gentle heat. On distilling the product, the acetic oxide passes over at 137° (H. Gal, *Compt. rend.* lvi. 360).—*β*. By the action of carbon bisulphide on lead or silver acetate:

$$2\left.\begin{matrix}(C^2H^3O)^2\\ Pb''\end{matrix}\right\}O^2 + CS^2 = 2PbS + CO^2 + 2(C^2H^3O)^2O.$$

A mixture of finely pulverised lead acetate, dried at 100°, and carbon bisulphide, is heated for some time to 165° in a strong sealed glass tube, of which it fills about a third, the tube being opened from time to time to permit the escape of carbonic acid gas. The liquid contents of the tube separated from the lead sulphide yield by distillation, first, the excess of carbon bisulphide, then a small quantity of acetic acid and a trace of acetone, and, lastly, acetic oxide, boiling at 137°. With silver acetate the reaction takes place more quickly.

Reactions.—According to A. Bauer (*Wien. Akad. Ber.* xliii. [2] 709; *Jahresb.* 1860, p. 438), acetic oxide heated to 100° in a sealed tube with *zinc-chloride* yields a product which separates by fractional distillation into acetic acid at 137°, and a residue which when freed by water from zinc-chloride, consists of a black-brown substance, C^4H^2O or $C^{20}H^{10}O^5$. The reaction is:

$$2C^4H^6O^3 = 2C^2H^4O^2 + H^2O + C^4H^2O.$$

Glacial acetic acid heated to 150°–160° with zinc-chloride suffers no alteration.

According to Schützenberger (*Jahresb.* 1863, p. 463), the mixture of acetic oxide and barium peroxide in anhydrous ether, used by Brodie for the preparation of acetyl peroxide (i. 55), gives off, when the barium peroxide is in excess and heat is applied, a large quantity of gas, consisting of 2 volumes carbon dioxide and 1 volume methyl (or ethyl-hydride), and leaves a residue of barium acetate:

$$2(C^2H^3O)^2O + BaO^2 = 2CO^2 + C^2H^6 + \left.\begin{matrix}(C^2H^3O)^2\\ Ba''\end{matrix}\right\}O^2.$$

Action of Chlorine, Bromine, and Iodine (H. Gal, *Ann. Ch. Phys.* [3] lxvi. 187).—When dry *chlorine gas* is passed into acetic oxide heated to 100°, acetyl chloride, boiling at 55°, passes over, and monochloracetic acid, boiling at 187°, remains:

$$(C^2H^3O)^2O + Cl^2 = C^2H^3OCl + \left.\begin{matrix}C^2H^2ClO\\ H\end{matrix}\right\}O.$$

A mixture of 2 at. *bromine* and 1 mol. acetic oxide becomes heated in a few minutes and yields similar products. *Iodine* does not act upon acetic oxide at 200°, but at higher temperatures the mass blackens and gives off hydriodic acid.

Dry *hydrochloric acid gas* acts strongly on acetic oxide at 100°, forming acetyl chloride and acetic acid:

$$(C^2H^3O)^2O + HCl + C^2H^3OCl + C^2H^4O^2.$$

Acetic oxide heated to 60° in a stream of carbonic acid gas with 2 mol. of *sulphuric chlorohydrate*, SO^3HCl, yields an acid, $C^2H^6SO^7$, which when converted into a lead-salt by neutralisation with lead carbonate, separated therefrom by hydrogen sulphide, and evaporated, remains as a thick syrup, solidifying in a vacuum to a hard crystalline, very deliquescent mass, insoluble in alcohol and ether. This acid is bibasic; its *potassium salt*, $C^2H^4K^2SO^7$, is very soluble in water and precipitated by alcohol as a granular powder. The *sodium salt*, $C^2H^4Na^2SO^7$, crystallises from water in crusts, from alcohol in concentric needles. The *silver salt*, $C^2H^4Ag^2SO^7$, is insoluble in alcohol and ether, moderately soluble in cold water, and separates from a concentrated solution of the acid mixed with silver nitrate and with alcohol, in large thin plates. The *barium salt*, $C^2H^4BaSO^7$, crystallises in nodular groups of hexagonal plates, and in crusts, insoluble in alcohol and ether, slightly soluble in cold, more freely in boiling water. The *lead salt* crystallises in white prisms.

When 2 mols. acetic oxide are heated with 1 mol. urea to the boiling point of the acetic oxide, the liquid, on cooling and addition of water, yields acetyl-urea, $CH^3(C^2H^3O)N^2O$ (Scheitz, Marsh a. Geuther, *Bull. Soc. Chim.* [2] x. 460).

Acetic oxide exerts no action on *oxamide*, even when the two are heated together to 140°–160° in a sealed tube (Scheitz, Marsh a. Geuther).

Acetic oxide treated with nascent *zinc-ethyl* (a mixture of 2 mol. ethyl iodide and 1 mol. acetic oxide, added by drops to pulverised zinc-sodium in a cooled vessel) yields methyl-ethyl-ketone:

$$\left.\begin{matrix}CH^3CO\\CH^3CO\end{matrix}\right\}O + Zn(C^2H^5)^2 = ZnO + 2CO\left\{\begin{matrix}CH^3\\C^2H^5.\end{matrix}\right.$$

The action is complete in twenty or thirty hours, and on adding potash to the product, drying the separated oil over fused potassium carbonate, rectifying, combining the portion which passes over between 100° with sodium bisulphite, and distilling the resulting crystalline compound with potassium carbonate, methyl-ethyl-ketone is obtained, boiling between 77° and 80°. With *methyl iodide* in like manner, common acetone (dimethyl ketone) is obtained (Saytzeff, *Zeitschr. f. Chem.* [2] vi. 104).

Action of Acetic oxide on Cellulose, Starch, &c.—According to Schützenberger (*Bull. Soc. Chim.* [2] v. 290), the etheroïdal compounds formed by cellulose, starch, sugar, &c., with acetic acid are formed more easily and abundantly by the use of acetic oxide, than by prolonged heating with glacial acetic acid, as recommended by Berthelot. The action of the acetic oxide usually begins at its boiling point, and when once set up, goes on spontaneously, yielding the new compound together with acetic acid. *Cellulose* is dissolved to a syrup at 160°. The resulting aceto-cellulose is white, solid, amorphous, insoluble in water and in alcohol, soluble in glacial acetic acid, and easily decomposed by alkalis, with reproduction of cellulose. *Starch* yields two compounds, one of which is insoluble in water, but soluble in alcohol and acetic acid; the other brittle, soluble in water and in alcohol; both are resolved by potash into acetic acid and dextrin. *Cane-sugar, glucose, milk-sugar, mannite, and dulcite* yield solid or glutinous bodies, having a bitter taste. *Glucosides* are acted upon by acetic oxide in a similar manner.

Compounds of Acetic oxide with Aldehydes (Geuther, *Jahresb.* 1860, p. 306, 1864, pp. 329, 334).—Acetic aldehyde unites with 1 and 2 molecules of acetic oxide, forming the compounds $C^2H^4O.C^4H^6O^3$ and $C^2H^4O.2C^4H^6O^3$. The first, described at p. 108, vol. i., is prepared by heating its components together in equivalent quantities to 180°. The second is formed by heating elaldehyde (i. 109) with acetic oxide to 160°. It is a liquid having a sp. gr. of 1·07 at 10°.

With acrolein, C^3H^4O, acetic oxide forms two compounds analogous in composition to those just described. The compound $C^3H^4O.C^4H^6O^3$ is obtained by heating of 1 molecule of acrolein and 1 molecule of acetic oxide in the water-bath for six hours, then washing the product with water and with sodium carbonate, and rectifying. It is also formed by heating one molecule of acrolein-chloride with 2 molecules of silver acetate to about 160°; but the transformation is never complete. The compound obtained by the first process is a liquid immiscible with water, and having a strong unpleasant fishy odour and very sharp taste; sp. gr. = 1·076 at 22°; boiling point, 180°. It slowly reduces silver in ammoniacal solution, and is resolved by potassium hydrate into acrolein and potassium acetate. The compound $C^3H^4O.2C^4H^6O^3$ is formed by heating metacrolein with acetic oxide to 150°; it is an oily liquid boiling at 180°.

With benzoic aldehyde.—When bitter almond oil is heated for some time to 150° with excess of acetic oxide, and the product is afterwards washed with water and potash, an oily liquid separates, which does not solidify if left to itself, even after a very long time; but on adding to it a particle of benzylic diacetate, it solidifies immediately to a crystalline mass melting at 44°–45°. This substance has the composition $C^{11}H^{12}O^4 = C^7H^6O + C^4H^6O^3$, and appears to be identical with the benzylic diacetate $C^7H^6(C^2H^3O^2)^2$, which Limpricht and Neubauer obtained by the action of benzylic chloride on silver acetate (Hübner, *Zeitschr. f. Chem.* [2] iii. 277).

Aceto-arsenious Oxide, $C^4H^6O^3.As^2O^3$ or $\left.\begin{matrix}C^2H^3O\\ AsO\end{matrix}\right\}O$, is produced by dissolving *arsenious oxide* in an equivalent quantity of acetic oxide at the boiling heat; the resulting syrupy liquid solidifies on cooling to a vitreous mass, which quickly absorbs moisture from the air, is resolved by water into acetic and arsenious acids, and decomposes at 220°, giving off a large quantity of carbon dioxide and traces of arsenious oxide, while acetic acid passes over and metallic arsenic remains in the retort.

Boric oxide dissolves slowly in acetic oxide, and the resulting vitreous mass, which is decomposed by water like the preceding compound, gives off acetic acid when heated, and leaves a residue soluble in water, which contains all the boric oxide employed.

When a mixture of acetic oxide and 'anhydrous tartaric acid' (insoluble tartaric anhydride, $C^4H^4O^5$, v. 691), is heated to 100°, the latter gradually dissolves, and a thick yellowish syrup is obtained, which begins to decompose at about 130°, giving off carbon dioxide and carbon monoxide; the same syrupy product is formed, together with lead-chloride, by the action of acetyl chloride on lead tartrate.

Vapour of *sulphuric oxide* (SO^3) is absorbed without blackening, by properly cooled acetic oxide, forming a yellowish gummy mass soluble in water. The solution neutralised with baryta-water and filtered from barium sulphate yields crystals of barium sulphacetate.

Aceto-hypobromous Oxide or **Anhydride.** *Acetate of Bromine,* $C^2H^3BrO^2 = \left.\begin{matrix}C^2H^3O\\ Br\end{matrix}\right\}O = CH^3.CO^2Br$.—This compound, isomeric with bromacetic acid, $CH^2Br.CO^2H$, appears to be formed by the action of bromine on the following compound; the product detonates after a few hours.

Aceto-hypochlorous Oxide or **Anhydride.** *Acetate of Chlorine,* $C^2H^3ClO^2 = \left.\begin{matrix}C^2H^3O\\ Cl\end{matrix}\right\}O = CH^3.CO^2Cl$ (Schützenberger, *Compt. rend.* lii. 359).—Isomeric with monochloracetic acid, $CH^2Cl.CO^2H$. Formed by passing gaseous hypochlorous oxide into cooled acetic oxide, which absorbs it completely:

$$(C^2H^3O)^2O + Cl^2O = 2(C^2H^3O)ClO.$$

On heating the resulting yellow liquid to 30°, to expel the excess of hypochlorous oxide, the hypochloracetic oxide remains as a very pale yellow liquid, having a strong irritating odour. It is not very stable, detonates violently at 100°, and can only be preserved in the dark and at a low temperature. It is decomposed by water, forming acetic and hypochlorous acids; also by most elementary bodies. Bromine and iodine eliminate the chlorine, and appear to take its place, but the resulting compounds cannot be isolated, the products often detonating spontaneously.

Aceto-cyanic Oxide. *Acetate of Cyanogen,* $C^3H^3NO^2 = CH^3.CO^2CN$, isomeric with cyanacetic and $CHCN.CO^2H$, is formed by the action of acetic chloride on silver cyanide, but it has not been isolated (ii. 297).

Aceto-hypo-iodous Oxides or **Anhydrides.** *Acetates of Iodine* (Schützenberger, *loc. cit.*; further, *Compt. rend.* liv. 1026; *Jahresb.* 1862, p. 240).—α. Iodine monoacetate, $C^2H^3IO^2$, is formed by the action of iodine monochloride on sodium acetate, but it cannot be separated from the other products of the reaction.—β. When iodine is gradually added to well-cooled chlorine acetate, it dissolves and expels the chlorine, and after a short time colourless crystals are formed, which under the influence of heat, water, or alcohol, react like the product α; but the mixture often detonates violently even on adding the first portions of iodine.

γ. Iodine triacetate, $I'''(C^2H^3O^2)^3$, is prepared by passing dry hypochlorous oxide into about 30 grams of acetic oxide containing in suspension 15 grams of pure and dry iodine, the liquid being well cooled. After a short time, yellowish needle-shaped crystals are formed, which afterwards disappear; and when the liquid has become perfectly colourless, it deposits colourless granular crystals of iodine acetate, which must be drained on a porous tile, and then freed from the last traces of acetic oxide by exposure to a current of dry air at 50°.

This compound, into which the iodine enters as a trivalent element, forms granular crystals, which on exposure to the air quickly acquire a rose colour changing to brown: they are deliquescent and instantly decomposed by water and by alcohol; quickly also when heated to 100°. Heated with acetic oxide, they yield iodine, carbon dioxide, and methylic acetate:

$$2I'''(C^2H^3O^2)^3 = 3CO^2 + I^2 + 3(CH^3)(C^2H^3O^2).$$

ACETOFORMOBENZOIC ETHER. See FORMOBENZOIC ACID.

ACETOGLYCERAL. See GLYCERALS.

ACETONE. C^3H^6O.—This compound is found in crude aniline, prepared from nitrobenzene, by the action of acetic acid and iron filings (C. G. Williams, *Chem. News*, ii. 231); and in diabetic urine (Petters, Kaulich a. Betz, *Jahresb.* 1861, p. 806). Anthon (*ibid.* 1860, p. 707) has observed its formation by spontaneous decomposition in a solution of grape-sugar.

The constitution of acetone as methyl-acetyl, $CH^3.C^2H^3O$, or dimethyl ketone, CH^3COCH^3, is clearly shown by its formation from zinc-methyl and acetyl chloride (Freund, *Ann. Ch. Pharm.* cxviii. 1):

$$Zn(CH^3)^2 + 2(CH^3.CO.Cl) = ZnCl^2 + 2(CH^3.CO.CH^3).$$

It is also produced by the action of sodium methylate on chloracetene or monochlorethylidene (Friedel, *Compt. rend.* lx. 930):

$$CH^3NaO + C^2H^3Cl = NaCl + CH^3.CO.CH^3.$$

Thirdly, by the action of aqueous hypochlorous acid and mercuric oxide on monobrominated or monochlorinated propylene, this reaction giving rise to monochloracetone, which is then converted into acetone by treatment with zinc and hydrochloric acid (Linnemann, *Bull. Soc. Chim.* [2] vi. 216):

$$2C^3H^5Cl + HgCl^2O^2 = HgCl^2 + 2C^3H^5ClO.$$

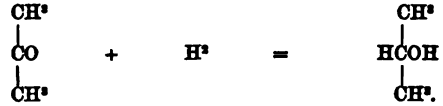
Fourthly, from the isomeric compound propylene oxide, by first treating that body with sodium amalgam, whereby it is converted into isopropyl alcohol, and then dehydrogenating the latter by treatment with sulphuric acid and potassium chromate (Linnemann, *Ann. Ch. Pharm.* cxl. 178):

$$\underset{\substack{\text{Propylene}\\\text{oxide.}}}{C^3H^6.O} + H^2 = \underset{\substack{\text{Isopropyl}\\\text{Alcohol.}}}{C^3H^8O}$$

and

$$\underset{\substack{\text{Isopropyl}\\\text{Alcohol.}}}{C^3H^8O} - H^2 = \underset{\text{Acetone.}}{C^3H^6O}$$

Reactions.—1. Acetone treated with *sodium-amalgam* and *water* takes up 2 at. hydrogen (which amounts to replacing the diatomic radical oxygen by the two monatomic radicals H and OH), and is converted into isopropyl alcohol (v. 889):



$$\begin{matrix} CH^3 \\ | \\ CO \\ | \\ CH^3 \end{matrix} \quad + \quad H^2 \quad = \quad \begin{matrix} CH^3 \\ | \\ HCOH \\ | \\ CH^3. \end{matrix}$$

2. By the action of *electrolytic oxygen*, as when a mixture of acetone and dilute sulphuric acid is subjected to the action of a feeble electric current (of three Bunsen's elements), acetone is converted into a mixture of acetic and formic acids, with evolution of carbon dioxide (Friedel, *Jahresb.* 1859, p. 338).—3. When 20 vols. acetone are cautiously mixed with 30 vols. *fuming nitric acid*, a considerable quantity of oxalic acid is produced. When 30 vols. acetone are gradually mixed with 10 vols. fuming nitric acid, and water is added before the reaction is completed, an oily body is precipitated, which, when treated with *ammonium sulphide*, is converted into a dark red product (*acetone-red*) soluble in water and in acids (Mulder, *J. pr. Chem.* xci. 472).

4. The action of *ammonia* and *carbon bisulphide* on acetone gives rise to sulphocarbonate and sulphocarbamate of acetonine (p. 29).

5. When acetone saturated with *hydrochloric acid gas* is left to itself for 8 to 14 days, and then mixed with water, a heavy brownish oil separates, consisting mainly of compounds of hydrochloric acid with mesityl oxide, $C^6H^{10}O(= 2C^3H^6O - H^2O)$, and phorone, $C^9H^{14}O(= 3C^3H^6O - 2H^2O)$ (Baeyer, *Ann. Ch. Pharm.* cxl. 297; *Jahresb.* 1866, p. 308). The mesityl-compound, $C^6H^{10}O.2HCl$ or $C^6H^{12}OCl^2$, heated with potassium cyanide, and then with potash, yields the potassium salt of a crystalline monobasic acid, $C^8H^{13}NO^3$:

$$C^6H^{12}OCl^2 + 2KCN = C^6H^{12}O(CN)^2 + 2KCl$$

and

$$C^6H^{12}O(CN)^2 + KHO + H^2O = NH^3 + C^8H^{12}KNO^3.$$

The phorone compound similarly treated is converted into a neutral nitrogenous body slightly soluble in boiling alcohol, from which it crystallises in shining plates, like naphthalene, sublimable at about 300° (Maxwell Simpson, *Proc. Roy. Soc.* xvi. 364).

6. With *hydriodic acid*, acetone yields iodopropylene, C^3H^5I, or an isomeric

compound; with *phosphorous iodide*, a solid together with two liquid iodides; with *hydrobromic acid* it yields merely isomeric modifications of acetone (Harnitz-Harnitzky, *Zeitschr. Ch. Pharm.* 1863, p. 416). According to Berthelot (*Bull. Soc. Chim.* [2] vii. 60), acetone treated with hydriodic acid yields propane, C^3H^8, together with water and iodine:

$$C^3H^6O + 4HI = C^3H^8 + H^2O + 2I^2.$$

7. When acetone is treated with *iodine* and *phosphorus*, and the product is dissolved in water and saturated with barium carbonate, a salt is obtained, having, according to E. Mulder (*Jahresb.* 1864, p. 329), the composition $Ba(C^3H^6PO^3)^2$. When decomposed by sodium carbonate, it yields the corresponding sodium salt, $NaC^3H^6PO^3$.

8. With *chloride of iodine*, acetone yields di-iodacetone, $C^3H^4I^2O$ (p. 28).

9. When *bromine* is gradually added to acetone, both liquids being cooled, the acetone takes up 2 at. bromine, forming the compound $C^3H^6O.Br^2$, which is a viscid liquid, heavier than water, and so unstable that it decomposes even at ordinary temperatures, giving off 1 or 2 molecules of hydrobromic acid, and yielding propionyl bromide, C^3H^5OBr, and its isomer, epibromhydrin, together with acrolein, C^3H^4O, and its hydrobromide, $C^3H^4O.HBr$. By repeatedly distilling the acetone bromide over caustic potash, there is obtained a mixture of acetone and epibromhydrin; and by distillation over lead oxide, a mixture of acetone and acrolein. With water and excess of silver oxide, acetone bromide yields (together with silver bromide) acrylic acid, or the products of its decomposition, formic and acetic acids. By slowly adding silver oxide to acetone bromide covered with water, silver bromide and propionic acid are formed, together with a small quantity of a body which dissolves in ether, crystallises therefrom in needles, and exhibits the characters of acrolein-hydrobromide (Linnemann, *Ann. Ch. Pharm.* cxxxv. 307). According to E. Mulder, on the other hand (*J. pr. Chem.* xci. 472), the direct action of bromine on acetone gives rise to substitution-products.

Acetone forms crystalline but unstable compounds with the acid sulphites of monamines. Ethereal solutions of acetone and *aniline bisulphite* deposit concentric groups of shining needles of the compound $C^6H^7N.H^2SO^3.C^3H^6O$, which, however, remain undecomposed only so long as they are immersed in ether saturated with sulphurous acid. Acetone forms a similar compound with the acid sulphite of *amylamine* (Schiff, *Zeitschr. f. Chem.* [2] iv. 12).

Bromacetones. *Monobromacetone*, C^3H^5BrO, identical with that which Riche obtained by the action of a feeble electric current on a mixture of acetone and hydrobromic acid (i. 31), is produced according to E. Mulder (*loc. cit.*) by treating acetone with less than an equivalent quantity [2 at. ?] of bromine.

On gradually adding 10 pts. bromine to 1 pt. of well-cooled acetone, a solid mass is obtained, which when washed with water, dissolved in alcohol, and reprecipitated by water, deposits first a mixture of tetra- and penta-brominated acetones, and afterwards prismatic and tabular crystals of *hydrated tetrabromacetone*, $C^3H^2Br^4O.2H^2O$. This compound is insoluble in water, soluble in alcohol, melts at 42° or 43°, gives off its water below 100°, and decomposes at a higher temperature.

Pentabromacetone, C^3HBr^5O, is obtained in colourless needles by adding 12 pts. bromine to 1 pt. acetone, dissolving the product in alcohol and adding water; the crystals melt at 75° (Mulder).

Chloracetones. These bodies are partly described in vol. i. *Monochloracetone*, C^3H^5ClO, produced by the electrolysis of a mixture of acetone and hydrochloric acid, is isomeric with epichlorhydrin. It is a mobile colourless liquid having a sp. gr. of 1·162 at 16°, and boiling at 119°. [Riche found the sp. gr. 1·14 at 14°, and the boiling point 117°.] It dissolves easily in alcohol and in ether, and in about 10 times its own bulk of water. It does not unite with alkaline bisulphites, is reconverted into acetone by zinc and hydrochloric acid, and when heated with moist silver oxide yields acetate and glycollate of silver, together with other products (Linnemann, *Ann. Ch. Pharm.* cxxxiv. 170).

Dichloracetone, $C^3H^4Cl^2O$, is produced by the action of phosgene on acetone; also by the action of chlorine on acetone containing a little iodine (Wroblewsky, *Zeitschr. f. Chem.* [2] iv. 565). It boils at 120°. It is decomposed by alcoholic solution of *potassium iodide*, with separation of potassium chloride and free iodine; the resulting liquid smells of acrolein, and contains a tarry volatile body which, in contact with aqueous ammonia, yields iodoform and acetamide. Dichloracetone boiled for two days with *phosphorus pentachloride*, is converted into dichloracetone chloride, $C^3H^4Cl^4$, isomeric with dichoropropylene chloride, $C^3H^4Cl^2.Cl^2$, and isomeric or identical with allylene tetrachloride:

$$C^3H^4Cl^2O + PCl^5 = PCl^3O + C^3H^4Cl^4.$$

This compound, purified by washing, drying, and distillation, is a colourless, oily liquid, having a not unpleasant odour, a sp. gr. of 1·47 at 13°, and boiling at 153°, or about 50° lower than dichloropropylene chloride. *Sodium* removes the whole of the chlorine, and eliminates allylene, C^3H^4 (Borsche a. Fittig, *Ann. Ch. Pharm.* cxxxiii. 111).

With *alcoholic potash* or *ammonia*, dichloracetone chloride, or allylene tetrachloride, is decomposed in the same manner as dichloropropylene dichloride, yielding isotrichloropropylene, $C^3H^3Cl^3$, an aromatic liquid boiling at 115°. *Chlorine* acts upon this latter compound, at ordinary temperatures and in diffused daylight, and on dichloracetone chloride when aided by water and sunshine, forming a solid sublimable body, $C^3H^3Cl^5$, which crystallises from alcohol in flocks of prismatic crystals (Borsche a. Fittig, *loc. cit.*).

Together with the dichloracetone dichloride, there is formed by the action of phosphorus pentachloride on dichloracetone (from admixed trichloracetone) a small quantity of trichloracetone chloride, $C^3H^3Cl^5$ (or chlorallylene tetrachloride)—isomeric with that just mentioned—which boils at 194°, and is also decomposed by alcoholic potash or ammonia, yielding tetrachloropropylene, $C^3H^2Cl^4$, boiling at 165° (Borsche a. Fittig).

According to E. Mulder (*Zeitschr. f. Chem.* [2] iv. 521), dichloracetone treated with *potassium sulphydrate* yields sulphacetone, C^3H^4SO, as a light yellow liquid, the alcoholic solution of which yields, with neutral lead acetate, a red amorphous body, $C^3H^6PbSO^3$, which may be regarded as a compound of PbS, with a body, $C^3H^6O^3$, isomeric with glucose. This body decolorises indigo in alcoholic solution. On heating acetone with excess of *chlorine*, then adding potash, and afterwards hydrochloric acid, also in excess, the odour of caramel becomes perceptible. With *potash* dichloracetone forms chiefly acetic and formic, no lactic acid. *Monochloracetone* treated with potash assumes a fine red colour, due to the formation of an acid called by Mulder acetone-carminic acid. Dichloracetone forms with *potassium cyanide* a crystalline precipitate, $3C^3H^4Cl^2O.CN.NH^4$, which gives with hydrochloric acid a compound, likewise crystalline, consisting of $C^9H^{12}Cl^6O^3$, designated by Mulder as isodichloracetone. Pentabromacetone forms with potassium sulphydrate a yellow amorphous body, C^3HBrS^2O (Mulder).

DI-IODACETONE. $C^3H^4I^2O = CO.(CH^2I)^2$ (Maxwell Simpson, *Laboratory*, p. 79).—Produced by gently heating acetone with an aqueous solution of iodine monochloride:

$$C^3H^6O + 2ClI = 2HCl + C^3H^4I^2O.$$

As soon as the temperature of the mixture rises to 70°, a violent action takes place, and di-iodacetone separates as a dark-coloured oil, which must be purified by washing with water and dilute potash, and drying over oil of vitriol. When pure it is a heavy straw-yellow oil, soon turning red from separation of iodine; it has a biting taste and smell, and attacks the skin. When heated with silver cyanide, it does not yield di-cyanacetone, but, as principal product, acrolein.

ACETONES. See KETONES.

ACETONIC ACID. $C^4H^8O^3 = \left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}COH.COOH$.—This acid, discovered by Städeler (*Ann. Ch. Pharm.* cxi. 320), and further examined by Morkownikoff (*ibid.* cxlvi. 339; *Bull. Soc. Chim.* [2] xi. 488), is produced—1. By the action of a mixture of hydrocyanic and hydrochloric acids upon acetone:

$$\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}CO + HCy = \left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}COH.CN.$$

$$\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}COH.CN + 2H^2O + HCl = NH^4Cl + \left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}COH.COOH.$$

2. From isobutyric acid, $\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}CH.COOH$, by introducing an atom of bromine into that acid, and, replacing the bromine by OH, by boiling the brominated acid with baryta. Morkownikoff, to whom this method is due, has shown that the *oxy-isobutyric acid*, thus produced, is identical with Städeler's acetonic acid; it is likewise identical with Frankland and Duppa's dimethoxalic acid (iv. 274).

To prepare acetonic acid, a mixture of acetone, hydrocyanic, and hydrochloric acids is left to itself for three weeks, then boiled for three days in a flask surmounted by a condenser, and finally evaporated till it no longer smells of acetone. To isolate the acetonic acid, the concentrated liquid is exhausted with ether, the ether is distilled off, and the remaining acid liquid is boiled with zinc carbonate, to convert it into zinc acetonate; and this salt, decomposed by hydrogen sulphide, yields acetonic acid, which when left to evaporate in a dry atmosphere crystallises to a pulp of rather long needles, which may be further purified by sublimation. It begins to sublime at 74°, melts at 79°, and solidifies at 75°. Oxyisobutyric acid exhibits the same properties (Morkownikoff). Acetonic acid distils with vapour of water; sulphuric acid does not attack it at ordinary temperatures, but decomposes it when heated, with evolution of gas, without, however, turning it brown. It is decomposed by hot caustic potash, apparently with formation of acetone. Its *ammonium salt* reduces silver nitrate after some time. The *barium salt* is crystallisable, soluble in water and alcohol, insoluble in ether. The *zinc* salt, $Zn(C^4H^7O^3)^2.2H^2O$, is slightly soluble in water, and crystallises in small hexagonal plates resembling the lactate (Städeler). The zinc salt of oxyisobutyric acid exhibits exactly the same properties (Morkownikoff).

ACETONINE. $C^9H^{18}N$.—Städeler obtained this biacid base by the action of ammonia on acetone (i. 32). Several of its salts have lately been prepared by E. Mulder (*J. pr. Chem.* ci. 401; *Jahresb.* 1867, p. 396), and by Mulder and Wefers Bettink (*J. pr. Chem.* ciii. 178; *Zeitschr. f. Chem.* [2] iv. 377).

The *sulphocarbamate*, $C^9H^{18}N^2.2CH^3NS^2$ or $C^9H^{20}N^2.2CH^2NS^2$, is produced by the action of ammonium sulphocarbamate on acetone:

$$2(NH^4)CH^2NS^2 + 3C^3H^6O = C^9H^{20}N^2.2CH^2NS^2 + 3H^2O.$$

It is soluble in water. The hydrochloride and other salts of acetonine may be prepared from it by the action of the corresponding acids. On evaporating its solution ammonium sulphocyanate remains behind.

The *sulphocarbonate*, $C^{10}N^{20}N^2S^3 = C^9H^{18}N^2.H^2CS^3$ or $C^9H^{20}N^2.CS^3$, is formed by the action of ammonium sulphocarbonate on acetone:

$$3C^3H^6O + (NH^4)^2CS^3 = C^9H^{20}N^2.CS^3 + 3H^2O.$$

This is the yellow body which Hlasiwetz obtained by treating acetone with ammonia and carbon bisulphide* (i. 19). It dissolves in acetone and in alcohol and exhibits in alcoholic solution the reactions of a sulphocarbonate. Heated with water or ammonia, it yields ammonium sulphocyanate, together with products of the decomposition of acetone.

Acetonine Hydrochloride, $C^9H^{18}N^2.2HCl$, or *Acetonium Chloride*, $C^9H^{20}N^2Cl^2$, is obtained in large crystals by precipitating the aqueous solution of the sulphocarbamate with mercuric chloride, filtering, passing hydrogen sulphide through the filtrate, again filtering, evaporating, treating the residue with alcohol, and leaving the alcoholic solution in the exsiccator over calcium chloride. Its solution forms with platinic chloride a crystallisable *platinochloride* easily soluble in water and in alcohol. The *sulphate* and *phosphate* are less easily crystallisable than the chloride. The *acetate* has but little stability, and is decomposed on evaporating its aqueous solution. The *oxalate*, $C^9H^{18}N^2.C^2H^2O^4$. 2aq., crystallises from water in large prisms.

When the aqueous solution of an acetonine salt is shaken up with potash and ether, the ether leaves on evaporation, not pure acetonine, but a yellowish easily decomposible liquid having an alkaline reaction.

ACETONITRATES. See ACETATES (p. 10).

ACETONITRILE. Syn. with METHYL CYANIDE. (See CYANIDES, ALCOHOLIC.)

ACETOPHOSPHORIC ACID. Syn. with ACETYLPHOSPHORIC ACID (iv. 595).

ACETOPYROPHOSPHORIC ACID. Syn. with ACETYLPYROPHOSPHORIC ACID (iv. 595).

ACETOSULPHURIC ACID. $C^2H^4SO^4$.—Syn. with SULPHACETYLENIC ACID (v. 475).

ACETOTOLUIDE. Syn. with TOLYLACETAMIDE (v. 871).

ACETOXACETIC ACID. Syn. with ACETYLGLYCOLLIC ACID. (See GLYCOLLIC ETHERS, ii. 917.)

ACETOXYBENZAMIC ACID. See OXYBENZAMIC ACID (iv. 291).

ACETULMIC ACID. $C^7H^{12}O^3$ (E. Hardy, *Bull. Soc. Chim.* [2] v. 339).—A mixture of acetone and chloroform treated with sodium yields the sodium-salt of chloracetulmic acid, $C^7H^{11}ClO^3$, an amorphous pulverulent substance which by boiling with soda is converted into acetulmic acid, and bioxyacetulmic acid. $2C^7H^{11}ClO^3 + 2KHO = 2KCl + C^7H^{12}O^2 + C^7H^{12}O^4$. These two acids separate as a bulky precipitate on neutralising the liquid with sulphuric acid. Acetulmic acid is described as a brown uncrystallisable, non-volatile substance insoluble in ether. Its chlorinated, brominated, and nitrated derivatives, described by Hardy, are likewise amorphous and non-volatile so that their formulæ cannot be regarded as determined with precision.

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* Ammonia and carbon bisulphide form by their mutual action, sulphocyanate, sulphocarbonate and sulphocarbamate of ammonium. The first of these has no action upon acetone; the second and third yield the products above mentioned.

ACETURIC ACID. $C^4H^7NO^3$ (Kraut and Hartmann, *Ann. Ch. Pharm.* cxxxiii. 99).—An acid produced by boiling acetic chloride with excess of the silver compound of glycocine:

$$C^2H^4AgNO^2 + C^2H^3OCl = AgCl + C^4H^7NO^3.$$

It forms small white crystals soluble in water, and not decomposed by boiling therewith. Its salts are soluble and crystallisable.

ACETYL. Wislicenus (*Zeitschr. f. Chem.* [2] iv. 681), by treating acetyl iodide with finely divided silver or copper, has obtained a colourless pungent liquid, which is probably free acetyl or diacetyl, $(C^2H^3O)^2$.

ACETYL ALCOHOL. $C^2H^4O = (C^2H^3)HO$; better called VINYL ALCOHOL (p. 37).

ACETYL BROMIDE, CHORIDE, &c. See ACETIC BROMIDE, CHLORIDE, &c. (pp. 20, 21).

ACETYL SULPHYDRATE and **SULPHIDE.** Syn. with THIACETIC ACID and ANHYDRIDE (v. 771, 772).

ACETYL-AMYL. $C^7H^{14}O = C^2H^3O.C^5H^{11}$. See KETONES.

ACETYL-ISOPROPYL. See PROPYL-COMPOUNDS.

ACETYLENE or **ETHINE.** C^2H^2.—This hydrocarbon is described in the ADDENDA to vol. i. p. 1111; but our knowledge of its properties has been largely increased by recent investigations. The name *acetylene* was given to it by Berthelot because it is related to the radicle C^2H^3, formerly called acetyl, in the same manner as ethylene to ethyl. *Ethine* is the name assigned to it in the systematic nomenclature of hydrocarbons proposed by Dr. Hofmann (*Proc. Roy. Soc.* xv. 57), and indicates its relation to ethane or ethyl hydride and ethene or ethylene:

C^2H^6	C^2H^4	C^2H^2
Ethane	**Ethene**	**Ethine**
(saturated).	**(bivalent).**	**(quadrivalent).**

Formation.—The formation of acetylene by direct combination of carbon and hydrogen takes place only under the influence of the electric arc; the most intense heat, even that produced by the sun's rays concentrated by a powerful lens, is unable to effect it; neither does the combination take place under the influence of the induction spark. To obtain acetylene in quantity under the influence of the electric arc, it is necessary to employ a powerful battery; with 40 or 50 Bunsen's elements 10 cub. cent. of acetylene may be obtained in a minute. The acetylene as it is formed is carried forward with the stream of hydrogen, and may be collected in an ammoniacal solution of cuprous chloride, and separated from the red precipitate thereby produced by the action of hydrochloric acid (p. 35). To obtain the acetylene quite pure, the charcoal forming the poles of the battery must be carefully purified from tarry matter, and traces of sulphur, iron, silicium, &c., by ignition in a current of chlorine (Berthelot, *Compt. rend.* lv. 640).

The following modes of production of acetylene have also been observed: *a.* By the incomplete combustion of hydrocarbons, and indeed of organic compounds in general. It may be shown to exist in the middle of the flame of pure ethylene gas (or of coal gas, previously freed from acetylene by passing through ammoniacal cuprous chloride) by drawing off the gases from that part of the flame through a tobacco-pipe stem connected with an aspirator. It is also formed in the imperfect combustion of a mixture of 1 vol. ethylene gas and 2 vols. chlorine (De Wilde, *Bull. Soc. Chim.* 1866, v. 172), Berthelot has devised an ingenious form of experiment by which the production of acetylene in the imperfect combustion of carbon compounds may be strikingly demonstrated. An ammoniacal solution of cuprous chloride is poured into a test-tube and spread over the inner surface; a small quantity of ether or other inflammable organic liquid is then introdued and set on fire, and the tube, held in an inclined position, is turned round slowly in the hand, so as to bring the burning ether as much as possible in contact with the cuprous solution; the characteristic red precipitate of the so-called cuprous acetylide is then immediately produced. A modification of this experiment has been devised by Mr. M'Leod, by which considerable quantities of acetylene may be readily obtained. The arrangement consists in burning a jet of oxygen in an atmosphere of marsh gas, and passing the products of combustion into ammoniacal cuprous chloride, the gases being continuously supplied, so that the process may go on without interruption. The marsh gas may further be replaced by coal gas, and the oxygen by atmospheric air (*Chem. Soc. J.* [2] iv. 152).

Acetylene is also produced in considerable quantity in the incomplete combustion of coal gas in a Bunsen's lamp, when the flame accidentally burns in the interior of the chimney. By placing over the chimney a funnel communicating with a series of bottles containing an ammoniacal silver solution, and finally with an aspirator, a considerable quantity of argentic acetylide may be collected. The formation of acetylene in this manner may be quickly demonstrated as a lecture experiment by inverting a flask over a Bunsen's lamp burning in the manner above mentioned, and afterwards pouring in a solution of cuprous chloride: the sides of the flask become covered with a thick film of the red copper compound (Riesh, *Zeitschr. f. Chem.* [2] iii. 598).

The incomplete oxidation of organic compounds at low temperatures, as when it is effected in the voltaic circuit, also gives rise to the formation of acetylene, as, for example, in the electrolysis of a solution of potassium aconitate or succinate (Berthelot, *Bull. Soc. Chim.* [2] ix. 103).

β. In the incomplete combustion of mixtures of hydrogen and gaseous or vaporous carbon-compounds not containing hydrogen, such as cyanogen, carbon monoxide, and carbon bisulphide. Such mixtures are not affected by heat, but on passing electric sparks through them acetylene is immediately formed. In the case of cyanogen an electrical apparatus of high tension must be used, as this gas offers great resistance to the passage of the spark. With carbon bisulphide there is a deposition of sulphur, which element also unites with the platinum terminals. In operating with a mixture of hydrogen and carbon monoxide, it is necessary to introduce a piece of caustic potash, slightly moistened on the surface, in order to absorb the carbon dioxide formed at the same time, which interferes with the further production of the acetylene (Berthelot, *Bull. Soc. Chim.* [2] v. 169).

γ. By exposing marsh gas to the action of a strong heat or to the spark of a powerful induction coil: $2CH^4 = C^2H^2 + 3H^2$ (Berthelot, *Compt. rend.* liv. 515). The action of the spark, which is rapid at first, diminishes as the volume of free hydrogen increases; but by absorbing the acetylene as fast as it is formed, about $\frac{4}{5}$ of the marsh gas may be ultimately transformed into acetylene. Coal gas may be used in this reaction instead of pure marsh gas, and Berthelot recommends the process in this form as the readiest mode of preparing acetylene. A portion of the acetylene is however polymerised during the process, being converted partly into benzene, $C^6H^6 = 3C^2H^2$, partly into black tarry hydrocarbons, which condense on the sides of the tube. A portion of the marsh gas undergoes a different decomposition, being completely resolved into carbon and hydrogen (Berthelot, *Bull. Soc. Chim.* [2] xi. 442).

According to De Wilde (*Bull. Soc. Chim.* [2] v. 267), the vapours of many other organic compounds, as ethylene, alcohol, ether, acetone, amyl alcohol, and especially benzene, likewise yield acetylene when induction sparks are passed through them.

δ. By passing the vapour of methyl chloride through a tube heated to low redness (Berthelot), or that of ethylene chloride through a tube heated to bright redness, hydrogen and marsh gas being produced at the same time, and carbon deposited (De Wilde, *Bull. Soc. Chim.* [2] v. 267). Amyl hydride from American petroleum passed through a red-hot iron tube yields, according to H. Vohl (*ibid.* [2] iv. 302), 20 p. c. acetylene. If this statement be correct, American petroleum should be the most productive source of acetylene.

ε. By passing a mixture of carbon monoxide and hydrochloric acid gas over red-hot magnesium silicide (Berthelot).

ζ. Styrol (cinnamene) passed through a red-hot tube is partly resolved into benzene and acetylene: $C^8H^8 = C^6H^6 + C^2H^2$ (Berthelot, *Jahresb.* 1866, p. 544).

η. Calcium carbide (produced from the alloy of zinc and calcium formed in contact with charcoal at a very high temperature) is converted by water into calcium hydrate and acetylene (Wöhler, *Ann. Ch. Pharm.* cxxiv. 220).

ι. The sodium salts of fumaric and maleic acid are decomposed by the action of the current in such a manner that acetylene (formed by oxidation) appears at the positive pole, and succinic acid (by reduction) at the negative pole (Kekulé, *Jahresb.* 1864, p. 389):

$$C^4H^2Na^2O^4 + H^2O = C^2H^2 + 2CO^2 + Na^2O + H^2,$$

and

$$\underset{\text{Fumarate.}}{C^4H^2NaO^4} + H^2 = \underset{\text{Succinate.}}{C^4H^4Na^2O^4}$$

Solubility.—At the temperature of 18°, water, carbon bisulphide, and amyl hydride dissolve about their own volume of acetylene; turpentine oil and carbon tetrachloride, 2 vols.; amyl alcohol and styrol, 3½ vols.; glacial acetic acid and absolute alcohol, nearly 6 vols. (Berthelot, *Ann. Ch. Phys.* [4] ix. 425).

Acetylene combines with the hæmoglobin of blood. (See BLOOD.)

Reactions.—1. Acetylene is decomposed by the induction-spark, with separation of charcoal.

2. *Action of Heat.*—When acetylene is heated to dull redness in a bent glass tube standing over mercury, it is gradually but completely converted, with separation of small quantities of carbon and hydrogen and formation of small quantities of ethylene and ethyl hydride, into a series of hydrocarbons polymeric with itself, namely: α. a very volatile liquid hydrocarbon, probably consisting of diacetylene, C^4H^4; β. benzene or triacetylene, C^6H^6, forming about half the entire product; γ. cinnamene, styrol, or tetracetylene, C^8H^8, boiling between 135° and 160°, and constituting about ⅓ of the whole; δ. a liquid mixture (distilling between 210° and 250°) of naphthalene and another hydrocarbon, probably pentacetylene or naphthalene hydride, $C^{10}H^{10}$; ε. a mixture of strongly fluorescent oils distilling at 250°–340°; ζ. retene or enneacetylene, $C^{18}H^{18}$, distilling at 360°, and crystallising in shining needles. The mode of decomposition is greatly influenced by the presence of foreign substances. If a piece of coke, ignited and cooled under mercury, be introduced into the bent glass tube, the acetylene is resolved, under the same conditions as above, into carbon and hydrogen, with scarcely any secondary products. In presence of iron the decomposition takes place more quickly and readily, the acetylene being then partly resolved into its elements, partly converted into other hydrocarbons, different from those above mentioned. When acetylene is slowly passed through a porcelain tube heated to bright redness, it is almost wholly resolved into carbon and hydrogen, the only secondary products being small quantities of ethylene and tar containing naphthalene.

3. *Action of Hydrogen.*—Hydrogen does not act upon acetylene at ordinary temperatures; but when the two gases are heated together, small quantities of ethylene, ($C^2H^4 = C^2H^2 + H^2$), and of benzene and other polymers of acetylene, are produced. The decomposition of acetylene by heat is retarded by the presence of hydrogen and of other gases, e.g. nitrogen, carbon monoxide, marsh gas, ethyl hydride; and hence it is that acetylene can be formed by the action of the electric arc on charcoal in an atmosphere of hydrogen, in spite of its tendency to split up into its elements at high temperatures.

By the action of nascent hydrogen on alkaline, but not on acid liquids, acetylene is converted into ethylene; this result may be obtained by the action of zinc and aqueous ammonia (which evolves hydrogen) on the so-called cuprous acetylide (p. 35).

When acetylene is mixed with excess of hydrogen in a jar standing over mercury, and a small quantity of platinum black enclosed in a spiral of platinum wire is introduced into the mixture, the gases combine in the proportion of 1 vol. acetylene to 2 vols. hydrogen, producing the saturated hydrocarbon, ethane or ethyl-hydride: $C^2H^2 + 2H^2 = C^2H^6$.

4. *Action of Hydrocarbons.*—When acetylene is heated to dull redness with an equal volume of *ethylene*, two-thirds of the mixture disappear in the course of half an hour, and a number of products are formed, the chief of which is a very volatile liquid, easily absorbed by bromine and by concentrated sulphuric acid, slightly soluble in ammoniacal cuprous chloride, and isomeric or identical with quartine or crotonylene, C^4H^6 (ii. 965). The two gases here unite in equal volumes with a condensation to one-half: C^2H^2 (2 vols.) + C^2H^4 (2 vols.) = C^4H^6 (2 vols.) (Berthelot, *Compt. rend.* lxii. 947). Acetylene heated with excess of *benzene* is quickly absorbed, scarcely one-fifth of the original volume being left, and on leaving the benzene to evaporate, a crystallised hydrocarbon is obtained, distinct from all known hydrocarbons. *Naphthalene* likewise absorbs acetylene, and more quickly than benzene; the gaseous residue in both these reactions consists of hydrogen mixed with small quantities of ethylene and ethyl hydride (Berthelot).

5. *Action of oxidising agents, etc.*—Acetylene, subjected at ordinary temperatures to the action of *potassium permanganate*, takes up oxygen, yielding oxalic acid, $C^2H^2 + O^4 = C^2H^2O^4$, formic and carbonic acids being also produced by a secondary reaction (Berthelot, *Compt. rend.* lxiv. 35). When passed through an ammoniacal solution of *cupric oxide*, acetylene is slowly absorbed, the greater part of it being oxidised, and at the same time there is deposited on the sides of the vessel a carbonaceous substance, mixed with a small quantity of cuprosovinyl oxide (Berthelot, *Ann. Ch. Phys.* [4] ix. 422).

6. *Action of Chlorine and Antimonic Chloride.*—Acetylene, either pure or mixed with other gases, sometimes detonates with chlorine, even in diffused daylight,

whether the chlorine or the acetylene is in excess, the products of the reaction being hydrochloric acid and free carbon. Frequently, however, no explosion takes place, but the two gases unite directly, forming the liquid dichloride $C^2H^2Cl^2$; sometimes, again, the action commences with the formation of this compound, and then the mixture suddenly explodes (Berthelot, *Bull. Soc. Chim.* [2] v. 191). When acetylene is prepared from cuprosovinyl oxide by the action of a large excess of hydrochloric acid, the hydrochloride C^2H^2HCl is constantly produced (Berthelot, *Compt. rend.* lviii. 978).

The chlorides of acetylene are best prepared by passing the gas into antimonic chloride, which absorbs it, with considerable evolution of heat, requiring the action to be regulated by moderate cooling. The nearly saturated liquid, on being left to cool, deposits large crystalline laminæ of the compound $C^2H^2SbCl^5$, which may be freed from excess of antimonic chloride by draining and evaporation, and dried in a stream of carbonic anhydride. This compound is very unstable, being instantly decomposed by water, and quickly resolved by heat into antimonious chloride, $SbCl^3$, and acetylene dichloride, $C^2H^2Cl^2$. If, however, it be dissolved in excess of antimonic chloride and then heated, a still more violent action takes place, resulting in the formation of acetylene tetrachloride:

$$C^2H^2SbCl^5 + SbCl^5 = 2SbCl^3 + C^2H^2Cl^4.$$

The dichloride is most easily prepared by heating the crude compound $C^2H^2SbCl^5$, containing a slight excess of antimonic chloride. A mixture of dichloride and tetrachloride of acetylene is then obtained, which may be separated by fractional distillation. The dichloride $C^2H^2Cl^2$ is a colourless mobile liquid, having a sweetish taste, and a powerful odour, like that of chloroform, which excites headache. It boils at 55°. It is altered by moist air, and slowly decomposed by water at 180° in sealed tubes, with formation of hydrochloric acid and condensed products. When heated by itself to 360° in a sealed tube for 100 hours, it is completely resolved into black laminar charcoal and hydrochloric acid.

The tetrachloride, $C^2H^2Cl^4$, is prepared, as above mentioned, by distilling the compound $C^2H^2SbCl^5$ with excess of antimonic chloride, the operation being conducted cautiously towards the end, to guard against explosion. It is a colourless liquid, resembling chloroform in taste and smell; boils at 147°; is slowly attacked by water with formation of hydrochloric acid. In an atmosphere of chlorine it is slowly converted into C^2Cl^6. When very cautiously treated with alcoholic potash it gives up 1 molecule of hydrochloric acid, and yields chlorinated acetylene dichloride, $C^2HCl.Cl^2$, a colourless liquid boiling at 88°. The tetrachloride is also decomposed by moisture. Heated to 300° for fifteen hours in a sealed tube, it is also resolved into hydrochloric acid and chlorinated acetylene dichloride. By prolonged heating to 360° for 100 hours, another molecule of hydrochloric acid is separated; but the residue consists, not, as might be expected, of carbon monochloride, C^2Cl^2, but of its polymeride, Julin's chloride of carbon or *perchlorobenzene*, C^6Cl^6, the formation of which from the C^2Cl^2 produced in the first instance, is precisely analogous to that of benzene from acetylene (Berthelot a. Jungfleisch, *Compt. rend.* lxix. 542; *Zeitschr. f. Chem.* [2] v. 680).

7. *Action of Bromine and Hydrobromic Acid.*—α. Pure acetylene slowly passed into a layer of bromine kept cold under water takes up 2 at. bromine, forming the dibromide $C^2H^2Br^2$, isomeric with dibromethylene. This compound, when purified, is a neutral, colourless, oily liquid, smelling like ethylene dibromide. It cannot be distilled, for when heated it undergoes a polymeric transformation, forming a product which cannot be volatilised without decomposition; nevertheless, the first drops which pass over at about 130° correspond nearly to the formula $C^2H^2Br^2$. Berthelot has recently found that the combination of acetylene with bromine requires the presence of light; on a foggy day he observed that acetylene was not sensibly absorbed by bromine; sometimes, even in bright diffused daylight, a mixture of acetylene and bromine vapour may remain for some minutes without combining, and then the reaction takes place suddenly. These facts are of importance with reference to the analysis of gaseous mixtures containing acetylene (*Bull. Soc. Chim.* [2] xi. 372).—β. When acetylene prepared from ether and not quite pure is passed in a rapid stream through liquid bromine, and the temperature allowed to rise, the tetrabromide $C^2H^2Br^4$ is produced. The latter compound was likewise obtained by Reboul (i. 1112). The two bromides which Perrot obtained in 1858 (*Compt. rend.* xlvii. 350) by combining with bromine the gases resulting from the decomposition of alcohol vapour by the electric spark, probably also consisted of the dibromide and tetrabromide of acetylene.—γ. With concentrated hydrobromic acid at 100°, acetylene forms a very volatile

hydrobromide, probably $C^2H^2.HBr$, which, like acetylene itself, is absorbed by ammoniacal cuprous chloride (Berthelot, *Bull. Soc. Chim.* [2] ii. 202).

Bromacetylene, C^2HBr, and its dibromide, C^2HBr^3 or C^2HBr,Br^2; already described in vol. i. p. 1112, are produced by the action of alcoholic potash on bromethylene dibromide, $C^2H^3Br.Br^2$. Bromacetylene is also formed, together with muconic acid, by boiling *mucobromic acid* (a product of the action of bromine on pyromucic acid, iv. 763) with excess of baryta-water:

$$\underset{\substack{\text{Mucobromic}\\\text{acid.}}}{2C^4H^2Br^2O^3} + H^2O = \underset{\substack{\text{Brom-}\\\text{acetylene.}}}{C^2HBr} + \underset{\substack{\text{Muconic}\\\text{acid.}}}{C^4H^2O^3} + 2CO^2 + 3HBr.$$

(Schmelz a. Beilstein, *Ann. Ch. Pharm. Suppl.* iii. 275).

8. *Action of Iodine and Hydriodic Acid.*—Acetylene does not combine with iodine at ordinary temperatures, even in sunlight. But when the two bodies are heated together to 100° in a closed flask for 15 to 20 hours, the di-iodide $C^2H^2I^2$ is obtained as a crystalline substance melting at 70° (Berthelot, *Bull. Soc. Chim.* [2] ii. 202).

When a concentrated solution of hydriodic acid is placed in contact with acetylene at ordinary temperatures, a mixture of acetylene mono-hydriodide, $C^2H^2.HI$, and dihydriodide, $C^2H^2.(HI)^2$, is produced, from which the former may be obtained pure by distillation with alcoholic potash. It is a colourless fragrant liquid, boiling at 62°, and isomeric with mono-iodethylene, C^2H^3I, which boils at 56° (Semenoff, *Compt. rend.* lxi. 646).

The dihydriodide, $C^2H^2.(HI)^2$, isomeric with ethylene iodide, $C^2H^4.I^2$, is obtained, according to Berthelot, by simply leaving concentrated hydriodic acid in contact with acetylene; according to Semenoff, only by heating the strong acid to 100° in contact with acetylene, and even then not quite free from mono-iodide. It is a liquid distilling without decomposition at 180° (Berthelot), and yielding acetylene when decomposed by alcoholic potash.

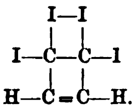
According to more recent experiments by Berthelot (*Bull. Soc. Chim.* [2] vii. 53; *Jahresb.* 1867, p. 344), the dihydriodide produced in the first instance is converted by further action of the hydriodic acid into ethane, C^2H^6:

$$C^2H^2 + 2HI = C^2H^4I^2;\ \text{and}\ C^2H^4I^2 + 2HI = C^2H^6 + 2I^2.$$

The compounds of acetylene with chlorine, bromine, and iodine above described show that acetylene is a tetratomic or quadrivalent radicle, but that, like all such radicles (tin, titanium, silicium, &c.), it is likewise capable of acting as a bivalent radicle, or rather of forming compounds containing 2 at. Cl, Br, &c., in which its combining capacity is only half saturated.

A tetra-iodide having the composition $C^4H^2I^4$, is produced by passing acetylene into an ethereal solution of iodine, or, better, by agitating argento-vinyl oxide, $(C^2HAg^2)^2O$, suspended in water, with ethereal solution of iodine till the latter is no longer decolorised. On distilling off the ether, the tetra-iodide is obtained as a yellow crystalline mass, having an extremely repulsive odour, volatilising even at ordinary temperatures, and melting at 74°, with decomposition and brown coloration. It dissolves easily in alcohol, ether, and carbon bisulphide, and when heated with alcoholic potash, gives off a large quantity of acetylene, and yields a small quantity of a very volatile oil, probably consisting of iodacetylene, C^2HI (Max Berend, *Ann. Ch. Pharm.* cxxxi. 122).

The iodide $C^4H^2I^4$ may be regarded as a compound of acetylene C^2H^2 with carbon di-iodide C^2I^4—these radicles being both bivalent, and saturating one another by their combination—or as a compound of 2 at. iodine with the bivalent radicle di-iododiacetylene, that is as $(C^4H^2I^2)''I^2$. Both these views are represented by the constitutional formula



$$\begin{array}{ccccccc} & & \mathrm{I} & - & \mathrm{I} & & \\ & & | & & | & & \\ \mathrm{I} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{I} \\ & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & = & \mathrm{C} & - & \mathrm{H}. \end{array}$$

The iodide is decomposed in ethereal solution by excess of *bromine*, yielding the compound $C^4Br^2I^2$ or $(C^4Br^2I^2)''IBr$:

$$(C^4H^2I^2)''I^2 + Br^6 = (C^4Br^2I^2)''IBr + 2HBr + IBr.$$

This bromiodide forms white crystals smelling like bromoform and melting at 100°. At a high temperature it decomposes with separation of iodine, and behaves to solvents in the same manner as the iodide $C^4H^2I^4$.

When a stream of *nitrous acid* vapour is slowly passed through a solution of the tetra-iodide in alcoholic ether, the latter being continually renewed, iodine separates, and the liquid, which has again become clear, yields on evaporation a residue which crystallises from alcohol or chloroform in white silky needles, corresponding in composition to the formula $[C^4H^4(NO^2)I]''I^2$. They are easily decomposed, even in a vacuum, giving off red vapours and leaving the compound C^2HI^3 (Berend, *Ann. Ch. Pharm.* cxxxv. 257).

9. *Action of Nitrogen.*—When a series of strong induction sparks is passed through a mixture of acetylene and nitrogen, the two gases unite and form hydrocyanic acid:

$$C^2H^2 + N^2 = 2CHN.$$

Carbon and hydrogen are at the same time set free by a secondary action, but this may be prevented by diluting the gaseous mixture with 10 times its volume of hydrogen. The formation of hydrocyanic acid goes on rapidly at first, but soon slackens, and after the passage of the sparks has been continued for an hour and a half, only about one-fifth of the volume of the mixed gases is found to be converted into hydrocyanic acid. In fact, a reverse action takes place at the same time, part of the hydrocyanic produced being again resolved into acetylene and nitrogen, and after a certain time this reverse action goes on as quickly as the production of the acid. But by introducing a small quantity of strong potash-solution, so as to absorb the hydrocyanic acid as fast as it is formed, the whole of the acetylene and nitrogen, if mixed in equal volumes, will ultimately be converted into hydrocyanic acid (Berthelot, *Compt. rend.* lxvii. 1141).

10. *Action of Metals.*—With the alkali-metals acetylene forms substitution-products. *Sodium* gently heated in the gas, melts and partly absorbs it, leaving a volume of hydrogen (with small quantities of ethylene and ethyl hydride) equal to about half the volume of the gas, and is converted into sodium-acetylene, C^2HNa. The reaction takes place according to the equations

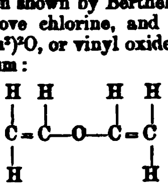
$$2C^2H^2 + Na^2 = 2C^2HNa + H^2$$
$$3C^2H^2 + Na^2 = 2C^2HNa + C^2H^4$$
$$5C^2H^2 + Na^4 = 4C^2HNa + C^2H^6.$$

At a dull red heat disodium-acetylene, C^2Na^2, is formed, with separation of a volume of hydrogen about equal to that of the original gas: $C^2H^2 + Na^2 = C^2Na^2 + H^2$. Both these compounds are decomposed by water, with formation of acetylene.

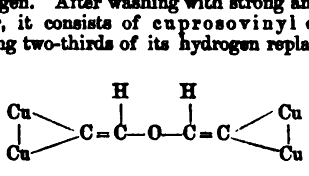
Potassium likewise decomposes acetylene, and much more violently than sodium; when melted in the gas it takes fire and is converted into dipotassium-acetylene, C^2K^2: the same compound is also formed in small quantity when potassium is heated to dull redness in ethylene gas: $C^2H^4 + K^2 = C^2K^2 + 2H^2$. Traces of it are found in commercial potassium.

Most other metals, except magnesium and iron, appear to be without action upon acetylene: iron decomposes it completely at a dull red heat, but does not unite with it (Berthelot, *Bull. Soc. Chim.* [2] v. 187).

11. *Action of Salts.*—*a.* The red precipitate produced by acetylene in an ammoniacal solution of cuprous chloride, and originally regarded as cuprosacetylene, C^2HCu', has been shown by Berthelot to contain oxygen. After washing with strong ammonia to remove chlorine, and then with water, it consists of cuprosovinyl oxide, $(C^2HCu^2)^2O$, or vinyl oxide, $(C^2H^3)^2O$, having two-thirds of its hydrogen replaced by cuprosum:



Vinyl oxide.



Cuproso-vinyl oxide.

Its formation is represented by the equation

$$2C^2H^2 + 2Cu^2Cl^2 + H^2O + 4NH^3 = 4NH^4Cl + (C^2HCu^2)^2O.$$

When heated with hydrochloric acid, it yields cuprous chloride and acetylene:

$$(C^2HCu^2)^2O + 4HCl = 2Cu^2Cl^2 + H^2O + 2C^2H^2.$$

On heating it with zinc and aqueous ammonia, the nascent hydrogen thereby evolved unites with the elements of the acetylene, producing ethylene:

$$(C^2HCu^2)^2O + 2H^2 = Cu^4 + H^2O + 2C^2H^2$$

and

$$C^2H^2 + H^2 = C^2H^4.$$

It is a very unstable compound; easily oxidised; detonates when struck or when heated to between 95° and 120°, producing water, copper, carbon, carbon dioxide, and traces of carbon monoxide. An ammoniacal solution of cuprous chloride is capable of detecting $\frac{1}{200}$ of a milligramme of acetylene mixed with hydrogen. In presence of air the delicacy of the reaction is limited to $\frac{1}{100}$ of a milligramme. It is important that the solution used be quite free from cupric salts, as these would oxidise the acetylene and interfere with the formation of the red compound (p. 32).

When a slow current of acetylene is passed into a concentrated solution of potassio-cuprous chloride, a yellow crystalline precipitate is formed, which, when washed with a strong solution of potassium chloride, and afterwards with water, leaves **cuprosovinyl chloride**, C^2HCu^2Cl, a compound of darker colour than the oxide; it forms double salts with the chlorides of the alkali-metals, and is converted by ammonia into the oxide. **Cuprosovinyl oxychloride** is formed by passing acetylene into a solution of cuprous chloride in hydrochloric acid slightly supersaturated with ammonia: it constitutes the chief portion of the crude red precipitate commonly called cuprous acetylene. The **bromide** and **oxybromide of cuprosovinyl** and the corresponding **iodine** and **cyanogen compounds** are formed by similar processes. A **basic cuprosovinyl sulphite** is formed by passing acetylene into an ammoniacal solution of cuprous sulphite; and black-brown **cuprosovinyl sulphide** is obtained, mixed with copper sulphide, by the action of sulphuretted hydrogen on the oxide (Berthelot, *Bull. Soc. Chim.* [2] v. 191; *Jahresb.* 1866, p. 510).

β. **Argentovinyl oxide**, $(C^2HAg^2)^2O$, is formed, exactly like the corresponding copper compound, by passing acetylene into an ammoniacal solution of silver nitrate. When it is suspended in water and treated with bromine, silver bromide is formed, and on distilling the liquid, two products are obtained, viz. an oil, C^2HBr^3, and beautiful white crystals, $C^2HBr^3.HBr$, melting at about 42°, having an agreeable odour, soluble in alcohol, ether, benzene, chloroform, and carbon bisulphide, and yielding acetylene when treated with reducing agents (Berend, *Ann. Ch. Pharm.* cxxxv. 257).

The two brominated compounds just mentioned are isomeric with those which Reboul obtained by the action of alcoholic potash on dibromethylene dibromide (i. 1112), but it is remarkable that they are inversely liquid or crystallised; thus:

Berend:	C^2HBr^3 liquid.	$C^2HBr^3.HBr$ crystallised.
Reboul:	C^2HBr^3 crystallised.	$C^2H^2Br^4$ liquid.

Argentovinyl chloride, C^2HAg^2Cl, is formed on passing acetylene into an ammoniacal solution of silver chloride, as a white curdy precipitate, which is decomposed by boiling hydrochloric acid, with evolution of acetylene; and by nitric acid, with oxydation of acetylene, separation of silver chloride, and solution of a quantity of silver equivalent to that of the silver chloride separated. With a boiling solution of sal-ammoniac it is decomposed in the manner shown by the equation:

$$C^2HAg^2Cl + NH^4Cl = C^2H^2 + 2AgCl + NH^3.$$

The *sulphate, phosphate* and *benzoate of argentovinyl* are obtained in a similar manner (Berthelot, *loc. cit.*).

Argentic bromacetylide is formed by the action of bromacetylene on ammoniacal silver nitrate. To prepare it, the vapours evolved by treating dibromethylene dibromide with boiling alcoholic potash (i. 1112) are passed into cold alcohol, which then retains in solution dibromethylene, bromacetylene, and small quantities of acetylene; and on diluting this solution with water and ammonia, and then dropping into it an ammoniacal solution of silver nitrate, an explosive precipitate is formed at first, and afterwards a crystalline precipitate. As soon as the latter appears, the solution is to be filtered, and the precipitation completed. The crystalline precipitate consists of **argentic bromacetylide** having the composition $(C^2BrAg)^2.AgBr.4H^2O$. It crystallises in silver-white needles, and detonates with violence by friction, or by contact with strong acids. When it is shaken up with an ethereal solution of iodine, the ether takes up a bromo-iodated compound, probably identical with the bromiodide of carbon, $C^4Br^2I^2$, previously described (p. 34) (Berend, *loc. cit.*).

γ. In a solution of *sodio-aurous hyposulphite* mixed with ammonia, acetylene produces at first a copious flocculent precipitate, regarded by Berthelot as **aurosovinyl oxide**, which, when dried, detonates violently by percussion, and explodes with flame; but the greater part of the aurous double salt remains undecomposed.

δ. **Mercurovinyl oxide** is produced when acetylene is left for some time in contact with a solution of potassio-mercuric iodide mixed with a little ammonia, and the resulting scaly crystalline precipitate is washed with a strong solution of potassium iodide to remove ammoniacal mercury-compounds; it then remains in the form of a white highly explosive powder (Berthelot).

When coal gas is passed through a solution of mercuric iodide in potassium iodide and potash, a yellow precipitate is formed, which, after drying, detonates slightly when heated, yielding a sublimate of mercury and mercuric iodide and a carbonaceous residue. Heated with dilute acids, it evolves a combustible gas exhibiting the characters of acetylene. By passing the gases from a Bunsen's burner through the solution of mercuric iodide, a light yellow, somewhat more explosive precipitate was formed, consisting of $C^2HHgI.HgO$ (Bassett, *Chem. News*, 1869, p. 28).

ε. The blue solution of *chromous sulphate* in sal-ammoniac and ammonia absorbs acetylene in large quantity, and is decolorised thereby; but after a while the liquid again becomes coloured, with separation of chromic oxide and evolution of ethylene. Berthelot explains this result by supposing that chromosovinyl oxide is at first produced, and then reacts with water, so as to form chromic oxide and ethylene:

$$2CrO + C^2H^2 + H^2O = Cr^2O^3 + C^2H^4.$$

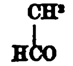
Acid solutions of chromous oxide do not absorb acetylene more abundantly than water, and the corresponding salts of the other metals of the iron group do not act upon acetylene, even in ammoniacal solution and in presence of sal-ammoniac; nevertheless, Berthelot regards the existence of analogous compounds as probable.

11. *Action of Sulphuric Acid.*—Acetylene agitated briskly, and for a long time, with strong sulphuric acid, unites with it, forming vinyl-sulphuric acid, $C^2H^4SO^4 = (C^2H^3)HSO^4$ or $\left.\begin{array}{c}(SO^2)''\\C^2H^3\\H\end{array}\right\}O^2$, originally, but less appropriately, called acetyl-sulphuric acid (i. 1112).

The acid liquid, distilled with water, yields vinyl alcohol (acetyl alcohol), $(C^2H^3)HO$, just as ethyl sulphuric acid yields ethyl alcohol:

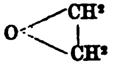
$$(C^2H^3)HSO^4 + H^2O = H^2SO^4 + (C^2H^3)HO.$$

This alcohol is monatomic and isomeric with aldehyde and with ethylene oxide. The difference of constitution of these three compounds may be represented by the following formulæ:

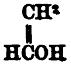


$\begin{array}{c}CH^3\\|\\HCO\end{array}$

Aldehyde.



Ethylene oxide.

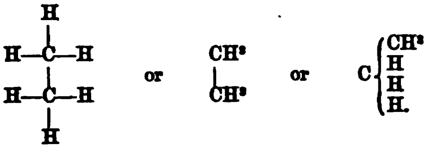


$\begin{array}{c}CH^2\\\|\\HCOH\end{array}$

Vinyl alcohol.

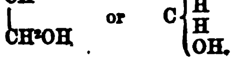
ACETYL-METHYL. Syn. with ACETONE.

ACIDS, ORGANIC. The general relations and constitution of organic acids are best understood by regarding them as derived from hydrocarbons containing even numbers of hydrogen atoms, through the medium of alcohols. Consider for example the saturated hydrocarbon ethane or ethyl hydride, C^2H^6. In this molecule each of the hydrogen atoms is directly associated with an atom of carbon, as shown by the formula:



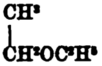
$$\begin{array}{c}H\\|\\H-C-H\\|\\H-C-H\\|\\H\end{array} \quad \text{or} \quad \begin{array}{c}CH^3\\|\\CH^3\end{array} \quad \text{or} \quad C\left\{\begin{array}{l}CH^3\\H\\H\\H.\end{array}\right.$$

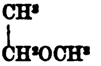
Now suppose one of these hydrogen atoms to be displaced by an atom of oxygen. This atom, being diatomic, will unite itself by one of its units of equivalence or affinity to the carbon; and by its other unit of affinity will retain the hydrogen which it has displaced, so that this hydrogen will still remain in the molecule united to the carbon, no longer directly, but through the medium of the oxygen, the final result being the same as if the hydrogen were replaced by an atom of oxyhydryl or hydroxyl, OH. The new molecule thus formed is ethyl-alcohol:

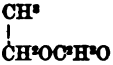


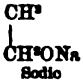
$$\begin{array}{c}CH^3\\|\\CH^2OH\end{array} \quad \text{or} \quad C\left\{\begin{array}{l}CH^3\\H\\H\\OH.\end{array}\right.$$

The hydrogen atom thus united to the carbon through the medium of oxygen is replaceable by alcohol-radicles, acid-radicles and alkali-metals, the products of such replacement being ethers: thus from ethyl-alcohol may be formed

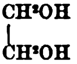

$$\begin{array}{l}CH^3\\ |\\ CH^2OC^2H^5\end{array}$$
Ethylic ethylate.

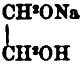

$$\begin{array}{l}CH^3\\ |\\ CH^2OCH^3\end{array}$$
Methylic ethylate.

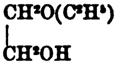

$$\begin{array}{l}CH^3\\ |\\ CH^2OC^2H^3O\end{array}$$
Ethylic acetate.

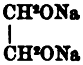

$$\begin{array}{l}CH^3\\ |\\ CH^2ONa\end{array}$$
Sodic ethylate.

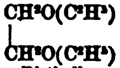
Now it is found that the number of times in which this replacement can take place, in other words, the number of ethers that an alcohol can form by substitution of any given acid- or alcohol-radicle for its hydrogen, is equal to the number of atoms of hydroxyl contained in its molecule. Thus, ethyl-alcohol, which contains but one atom of hydroxyl, can form but one set of ethers, viz. neutral ethers like those above formulated; but an alcohol containing two or more atoms of hydroxyl can form unsaturated as well as saturated ethers, thus:

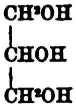

$$\begin{array}{l}CH^2OH\\ |\\ CH^2OH\end{array}$$
Ethylene alcohol.

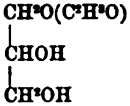

$$\begin{array}{l}CH^2ONa\\ |\\ CH^2OH\end{array}$$
Sodic ethylenate.

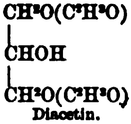

$$\begin{array}{l}CH^2O(C^2H^5)\\ |\\ CH^2OH\end{array}$$
Ethylic ethylenate.

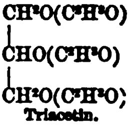

$$\begin{array}{l}CH^2ONa\\ |\\ CH^2ONa\end{array}$$
Disodic ethylenate.


$$\begin{array}{l}CH^2O(C^2H^5)\\ |\\ CH^2O(C^2H^5)\end{array}$$
Diethylic ethylenate.


$$\begin{array}{l}CH^2OH\\ |\\ CHOH\\ |\\ CH^2OH\end{array}$$
Glycerin.


$$\begin{array}{l}CH^2O(C^2H^3O)\\ |\\ CHOH\\ |\\ CH^2OH\end{array}$$
Monoacetin.


$$\begin{array}{l}CH^2O(C^2H^3O)\\ |\\ CHOH\\ |\\ CH^2O(C^2H^3O)\end{array}$$
Diacetin.

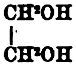

$$\begin{array}{l}CH^2O(C^2H^3O)\\ |\\ CHO(C^2H^3O)\\ |\\ CH^2O(C^2H^3O)\end{array}$$
Triacetin.

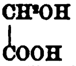
The number of hydrogen atoms thus replaceable by alcoholic or acid radicles, or by alkali-metals, determines what is called the atomicity of the alcohol. *An alcohol containing* n *atoms of hydroxyl is said to be* n-*atomic.*

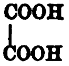
In an alcohol, however, the hydrogen is never replaced by metals by way of double decomposition with metallic hydrates or oxides, in the same manner as in an acid; in other words, alcohols do not form true metallic salts. The only metals that can replace the hydrogen in them are the alkali-metals, which decompose them as they decompose water, by direct displacement.

To convert the alcohol into an acid, a molecule of hydrogen in immediate connection with at least one atom of hydroxyl, OH, must be replaced by an atom of oxygen; in other words, one at least of the groups CH^2OH in the alcohol must be converted into COOH or CO^2H, called carboxyl or oxatyl; the hydrogen of the hydroxyl then becomes replaceable by metals, so as to form salts by double decomposition, in the same way as in mineral acids; in other words, it becomes basic; thus ethyl alcohol, $\begin{array}{l}CH^3\\ |\\ CH^2OH,\end{array}$ is in this manner converted into acetic acid, $\begin{array}{l}CH^3\\ |\\ COOH\end{array}$ or $CH^3.CO^2H$.

Now it is clear that a monatomic alcohol can yield but one acid, and that this acid must be monobasic, like acetic acid. But a diatomic alcohol may be converted by oxidation either into a monobasic acid, by substitution of O for H^2, or into a bibasic acid by substitution of O^2 for H^4; thus:


$$\begin{array}{l}CH^2OH\\ |\\ CH^2OH\end{array}$$
Ethylene alcohol.


$$\begin{array}{l}CH^2OH\\ |\\ COOH\end{array}$$
Glycollic acid (monobasic).


$$\begin{array}{l}COOH\\ |\\ COOH\end{array}$$
Oxalic acid (bibasic).

The hydrogen of the hydroxyl in the groups CH^2OH, in which the substitution of O for H^2 has not taken place, still retains its alcoholic character, that is to say, its replaceability by acid or alcoholic radicles to form ethers. Hence it follows that the atomicity of an organic acid is the same as that of the alcohol from which it is derived, but its basicity may be either equal to or less than the atomicity. In other words, *an* n-*atomic alcohol may yield a series of acids all of* n-*atomicity, but of basicity equal to or less than* n.

The law that the basicity of an organic acid is equal to the number of atoms of carboxyl, CO^2H, that it contains—in other words, that an organic acid containing *n* atoms of carboxyl is *n*-basic—is a result of observation, and we are not at present able to give a satisfactory account of it on theoretical principles; but it is probable that the entrance of the electro-negative oxygen into the group COOH renders it more disposed than before to take up an electro-positive element such as a metal. For a complete understanding of the matter we must perhaps wait for an exact determination of the quantities of heat evolved in the several changes. At all events, the law above mentioned, that an organic acid containing *n*-atoms of carboxyl is *n*-basic, holds good in all cases. It is true there is one apparent exception to it, viz. carbonic acid, which is bibasic, and yet contains but one atom of carboxyl, being represented by the formula

$$OH.CO^2H \text{ or } C\left\{\begin{matrix}OH\\ O\\ OH\end{matrix}\right.$$

but from the last formula it is clear that the middle atom of oxygen may be considered as attached to either of the groups OH just as well as to the other, and therefore that the exception to the rule is only apparent.

On these principles organic acids may be classified as follows (see table, p. 53, vol. i.).

I. Monatomic Acids.

Fatty or Adipic Series. $C^nH^{2n}O^2 = C^{n-1}H^{2n-1}.CO^2H$.—The modes of formation and transformation of these acids are for the most part described in vol. i. pp. 50, 51. We have here to add the mode of formation discovered by Harnitz-Harnitzky (*Ann. Ch. Pharm.* cxxxv. 121), which consists in forming the corresponding chlorides by the action of carbonyl chloride (phosgene) on hydrocarbons of the marsh-gas series (paraffins), e.g.,

$$\underset{\text{Methane}}{CH^4} + \underset{\text{Phosgene}}{COCl^2} = HCl + \underset{\text{Acetyl-chloride}}{C^2H^3OCl}$$

$$\underset{\text{Quartane}}{C^4H^{10}} + \underset{\text{Phosgene}}{COCl^2} = HCl + \underset{\text{Valeryl-chloride,}}{C^5H^9OCl}$$

and converting these chlorides into acids by the action of water.

The following methods afford the means of building up the fatty acids and the corresponding alcohols, starting from methyl alcohol:—

Sodium methide treated with carbon dioxide yields sodium acetate (Wanklyn):

$$CH^3Na + CO^2 = CH^3.CO^2Na;$$

sodium acetate subjected to dry distillation with sodium formate yields acetic aldehyde:

$$\underset{\text{Sodium acetate}}{CH^3.COONa} + \underset{\substack{\text{Sodium}\\ \text{formate}}}{H.COONa} = \underset{\substack{\text{Sodium}\\ \text{carbonate}}}{CO(ONa)^2} + \underset{\text{Aldehyde;}}{CH^3.COH}$$

and acetic aldehyde heated with water and sodium-amalgam takes up hydrogen and is converted into ethyl-alcohol: $C^2H^4O + H^2 = C^2H^6O$. From ethyl-alcohol, sodium ethyl, C^2H^5Na, may be obtained (iv. 223); this may be converted into sodium propionate, from which by distillation with sodium formate, propionic aldehyde, $C^2H^5.COH$, should be obtained, and thence propylic alcohol, &c. &c. The passing from an alcohol $C^nH^{2n+2}O$ to the next higher fatty acid, $C^{n+1}H^{2n+2}O^2$, may also be effected by the action of alkalis or acids on the cyanides of the alcohol radicles (i. 50), the other stages of the process being the same as above described. It must be observed, however, that the formation of an aldehyde by distilling the salt of the corresponding fatty acid with a formate cannot be expected to be realised very high up in the series. Lieben a. Rossi have, however, made propionic, butyric, and valeric aldehydes by this process.

The fatty acids are distinguished by a remarkable degree of stability. Even some of the highest members of the series, viz. palmitic, stearic, and cerotic acid, may be distilled without alteration, and all of them, except formic acid, offer considerable resistance to the action of oxidising agents. According to Chapman a. Thorp (*Chem. Soc. J.* [2] iv. 477), acetic, propionic, valeric, and caproic acids are not attacked at 100° by a mixture of *potassium dichromate* and *sulphuric acid* containing 3, 5, or 8 p. c. of the dichromate, and in such proportions as to produce chromic sulphate and acid potassium sulphate, even when the action is continued for 24 hours in sealed tubes. At 130°, however, they undergo a certain amount of oxidation, which is accelerated by the presence of a large excess of strong sulphuric acid, or of free chromic acid, or of manganese dioxide, but does not take place at all when phosphoric acid is used instead of sulphuric acid. Dilute solutions of *permanganic acid* act like the chromic acid mixture, producing no oxidation of acetic or propionic acid, even at the boiling heat, and acting but slowly on formic acid in presence of sulphuric acid at ordinary temperatures; concentrated solutions, however, decompose these acids with facility.

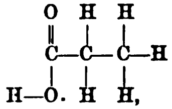
According to O. Veiel (*Ann. Ch. Pharm.* cxlviii. 160), the fatty acids are converted by oxidation with manganese dioxide and dilute sulphuric acid into one or more compound ethers, which contain alcohol-radicles lower in the carbon series than the acid itself, and yield the original acid by saponification; thus butyric acid yields a number of butyric ethers containing alcohol-radicles with less than 4 at. carbon, the principal product being propyl butyrate, $C^4H^7O^2.C^3H^7$. Valeric acid treated in like manner yields methyl valerate.

For the methods of converting the fatty acids into alcohols, see ALCOHOLS.

Isomerism among the Fatty Acids.—The first three acids of the series $C^nH^{2n}O^2$, do not admit of isomeric modifications. In fact, on looking at the constitutional formula of propionic acid, $C^3H^6O^2$, viz.,

$$C\left\{\begin{array}{l}CH^2CH^3\\O''\\OH\end{array}\right.$$

or



it is clear that so long as the type of an organic acid is preserved, that is, of an alcohol-radicle combined with carboxyl, no other arrangement of the carbon-atoms is possible; still less can this be the case with acetic or formic acid. But in the higher acids of the series isomeric modifications may exist. Thus the formula of butyric acid, $C^4H^8O^2$ or $C^3H^7.CO^2H$, may take either of the two forms

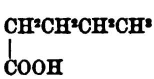
$$C\left\{\begin{array}{l}CH^2CH^2(CH^3)\\O''\\OH\end{array}\right. \qquad C\left\{\begin{array}{l}CH(CH^3)^2\\O''\\OH\end{array}\right.$$

Normal butyric acid Isobutyric acid,

the first containing normal propyl, the second isopropropyl (v. 887).

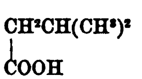
These two acids are produced by the oxidation of normal butylic alcohol or propyl carbinol, and isobutylic alcohol or isopropyl carbinol (the butylic alcohol of fermentation), respectively; also by the action of alcoholic potash on normal propyl cyanide and isopropyl cyanide respectively. Normal butyric acid is further produced by the fermentation of sugar in contact with putrid cheese (i. 691). The two acids exhibit considerable differences of physical and chemical character. In general the derivatives of normal butyric acid have higher specific gravities and boiling points than the corresponding derivatives of isobutyric acid. The latter is also more easily oxidised than normal butyric acid. (See BUTYRIC ACIDS.)

Of valeric acid, $C^5H^{10}O^2$, four isomeric forms are possible, viz.,



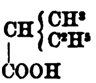
$$\begin{array}{l}CH^2CH^2CH^2CH^3\\|\\COOH\end{array}$$

Propyl-acetic acid.



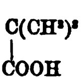
$$\begin{array}{l}CH^2CH(CH^3)^2\\|\\COOH\end{array}$$

Isopropyl acetic acid.



$$\begin{array}{l}CH\left\{\begin{array}{l}CH^3\\C^2H^5\end{array}\right.\\|\\COOH\end{array}$$

Methyl-ethyl acetic acid.



$$\begin{array}{l}C(CH^3)^3\\|\\COOH\end{array}$$

Trimethyl acetic acid.

The first and second of these modifications are produced by oxidation of the corresponding amylic alcohols; the third is not known, the fourth has quite recently been obtained by Butlerow (*Zeitschr. f. Chem.* [2] vi. 243) from tertiary butyl alcohol, $C(CH^3)^3.OH$. The optically active and inactive varieties of amyl alcohol yield by oxidation two varieties of valeric acid, exhibiting corresponding differences of optical character, and differing also slightly in boiling point; but these acids, like the alcohols from which they are derived, are probably only physically isomeric, not metameric. (See AMYL ALCOHOLS.)

The higher terms of the fatty acid series are of course susceptible of a still greater number of metameric modifications; but the only one in which such modifications have hitherto been observed is caprylic acid, $C^8H^{16}O^2$ (*q. v.*).

Acrylic Series. $C^nH^{2n-2}O^2$.—This series comprises two isomeric groups of acids; the one consisting of acids occurring in the vegetable or animal organism, or obtained from natural products by special processes, mostly by saponification of natural fats, e.g. oleic acid from olein; the other of acids formed by a general synthetical process. The acids of the first group are called **normal acrylic acids**; those of the second, **iso-acrylic acids.**

a. Normal Acrylic Acids.—The following are the known acids of this group:—

Acrylic acid	$C^3H^4O^2$	Physetoleic acid Hypogæic acid Gaïdic acid	$C^{16}H^{30}O^2$
Crotonic acid	$C^4H^6O^2$		
Angelic acid	$C^5H^8O^2$		
Pyroterebic acid	$C^6H^{10}O^2$	Oleic acid Elaïdic acid	$C^{18}H^{34}O^2$
? Damaluric acid	$C^7H^{12}O^2$		
? Damolic acid	$C^{13}H^{24}O^2$	Doeglic acid	$C^{19}H^{36}O^2$
Moringic acid Cimicic acid	$C^{15}H^{28}O^2$	Brassic acid Erucic acid	$C^{22}H^{42}O^2$

Most of these acids are oily liquids. When fused with *potassium hydrate* they yield the potassium-salt of acetic acid and of another acid of the fatty series with elimination of hydrogen, thus:

$$\underset{\text{Acrylic acid.}}{C^3H^4O^2} + 2KOH = \underset{\text{Acetate.}}{C^2H^3KO^2} + \underset{\text{Formate.}}{CHKO^2} + H^2$$

$$\underset{\text{Angelic acid.}}{C^5H^8O^2} + 2KOH = \underset{\text{Acetate.}}{C^2H^3KO^2} + \underset{\text{Propionate.}}{C^3H^5KO^2} + H^2$$

$$\underset{\text{Oleic acid.}}{C^{18}H^{34}O^2} + 2KOH = \underset{\text{Acetate.}}{C^2H^3KO^2} + \underset{\text{Palmitate.}}{C^{16}H^{31}KO^2} + H^2.$$

Generally:

$$C^nH^{2n-2}O^2 + 2KOH = C^2H^3KO^2 + C^{n-2}H^{2n-5}KO^2 + H^2.$$

They are also converted into fatty acids by the action of nascent hydrogen; e.g.,

$$\underset{\text{Crotonic acid.}}{C^4H^6O^2} + H^2 = \underset{\text{Butyric acid.}}{C^4H^8O^2}$$

β. Iso-acrylic Acids.—These acids, discovered by Frankland and Duppa (*Chem. Soc. J.* [2] iii. 133), are produced by abstraction of the elements of water from certain acid ethers derived from oxalic acid, $\begin{array}{l}COOH\\ |\\ COOH\end{array}$ or $\begin{array}{l}C\\ |\\ C\end{array}\left\{\begin{array}{l}OH\\ O\\ \hline O\\ OH\end{array}\right.$, by substitution of two atoms of an alcohol-radicle of the series C^nH^{2n+1} for one atom of oxygen (iv. 272), viz.,

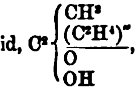
$$\underset{\text{Oxalic acid.}}{C^2\left\{\begin{array}{l}OH\\ O''\\ \hline O''\\ OH\end{array}\right.} \qquad \underset{\text{Dimethoxalic acid.}}{C^2\left\{\begin{array}{l}OH\\ (CH^3)^2\\ \hline O''\\ OH\end{array}\right.} \qquad \underset{\text{Ethomethoxalic acid.}}{C^2\left\{\begin{array}{l}OH\\ (CH^3)(C^2H^5)\\ \hline O''\\ OH\end{array}\right.} \qquad \underset{\text{Diethoxalic acid.}}{C^2\left\{\begin{array}{l}OH\\ (C^2H^5)^2\\ \hline O''\\ OH\end{array}\right.}$$

Now, when the ethylic ethers of these acids are treated with phosphorous chloride they give up the elements of a molecule of water, (H^2O), at the expense of one of the atoms of hydroxyl, OH, and of an atom of hydrogen abstracted from one of the monad alcohol-radicles, which is thereby converted into a dyad radicle (an olefine, C^nH^{2n}) capable of saturating the unit of equivalence of the carbon-atom left free by abstraction of the hydroxyl. The product is the ethylic ether of an isoacrylic acid; thus:

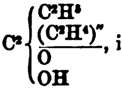
$$\underset{\text{Ethylic dimethoxalate.}}{C^2\left\{\begin{array}{l}OH\\ (CH^3)^2\\ \hline O\\ OC^2H^5\end{array}\right.} - H^2O = \underset{\text{Ethylic methacrylate.}}{C^2\left\{\begin{array}{l}CH^3\\ CH^{2\prime\prime}\\ \hline O\\ OC^2H^5\end{array}\right.}$$

The ethylic ether thus formed is converted into methacrylic acid by saponification with potash in the usual way. In this manner the following isoacrylic acids have been obtained:—

Methacrylic acid, $C^2\left\{\begin{array}{l}CH^3\\ (CH^2)''\\ \hline O\\ OH\end{array}\right.$, isomeric with Crotonic acid.

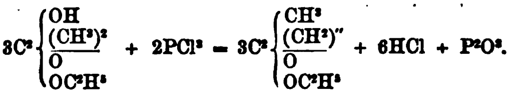


Methylcrotonic acid, $C^2\left\{\begin{array}{l}CH^3\\ \underline{(C^2H^4)''}\\ O\\ OH\end{array}\right.$, isomeric with Angelic acid.



Ethylcrotonic acid, $C^2\left\{\begin{array}{l}C^2H^5\\ \underline{(C^2H^4)''}\\ O\\ OH\end{array}\right.$, isomeric with Pyroterebic acid.

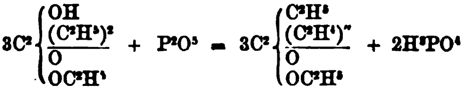
The actual formation of the ethers of these acids by the action of phosphorous chloride on the oxalic ethers above mentioned takes place as shown by the equation



$$3C^2\left\{\begin{array}{l}OH\\ \underline{(CH^3)^2}\\ O\\ OC^2H^5\end{array}\right. + 2PCl^3 = 3C^2\left\{\begin{array}{l}CH^3\\ \underline{(CH^2)''}\\ O\\ OC^2H^5\end{array}\right. + 6HCl + P^2O^3.$$

Ethylic dimethoxalate. Ethylic methacrylate.

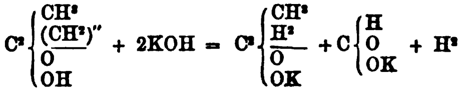
The transformation may also be effected by phosphoric anhydride, in which case the reaction is like the following:



$$3C^2\left\{\begin{array}{l}OH\\ \underline{(C^2H^5)^2}\\ O\\ OC^2H^5\end{array}\right. + P^2O^5 = 3C^2\left\{\begin{array}{l}C^2H^5\\ \underline{(C^2H^4)''}\\ O\\ OC^2H^5\end{array}\right. + 2H^3PO^4$$

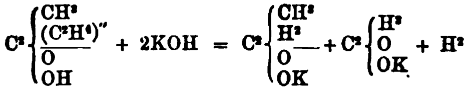
Ethylic diethoxalate. Ethylic ethylcrotonate. Metaphosphoric acid.

The isoacrylic acids fused with potassium hydrate are converted, like the normal acids, into two acids of the acetic series. The dyad radicle of the isoacrylic acids is replaced by two atoms of hydrogen derived from two molecules of potassium hydrate, (2KOH), and enters into combination with two atoms of oxygen; and at the same time the two atoms of potassium displace the basic hydrogen-atoms of the two fatty acids thus produced, converting them into potassium salts and expelling the hydrogen as gas; thus:



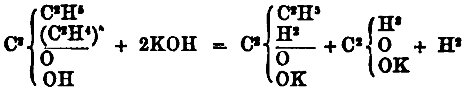
$$C^2\left\{\begin{array}{l}CH^3\\ \underline{(CH^2)''}\\ O\\ OH\end{array}\right. + 2KOH = C^2\left\{\begin{array}{l}CH^3\\ \underline{H^2}\\ O\\ OK\end{array}\right. + C\left\{\begin{array}{l}H\\ O\\ OK\end{array}\right. + H^2$$

Methacrylic acid. Propionate. Formate.



$$C^2\left\{\begin{array}{l}CH^3\\ \underline{(C^2H^4)''}\\ O\\ OH\end{array}\right. + 2KOH = C^2\left\{\begin{array}{l}CH^3\\ \underline{H^2}\\ O\\ OK\end{array}\right. + C^2\left\{\begin{array}{l}H^3\\ O\\ OK\end{array}\right. + H^2$$

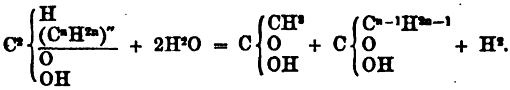
Methylcrotonic acid. Propionate. Acetate.



$$C^2\left\{\begin{array}{l}C^2H^5\\ \underline{(C^2H^4)''}\\ O\\ OH\end{array}\right. + 2KOH = C^2\left\{\begin{array}{l}C^2H^3\\ \underline{H^2}\\ O\\ OK\end{array}\right. + C^2\left\{\begin{array}{l}H^3\\ O\\ OK\end{array}\right. + H^2$$

Ethylcrotonic acid. Butyrate. Acetate.

The normal acrylic acids are decomposed by potash in a similar manner, yielding two acids of the series $C^nH^{2n}O^2$; but one of these is always acetic acid; hence it is inferred that they have a constitution represented by the formula $CH(C^nH^{2n})''.CO^2H$, and that their decomposition by alkalis takes place in the manner represented by the equation



$$C^2\left\{\begin{array}{l}H\\ \underline{(C^nH^{2n})''}\\ O\\ OH\end{array}\right. + 2H^2O = C\left\{\begin{array}{l}CH^3\\ O\\ OH\end{array}\right. + C\left\{\begin{array}{l}C^{n-1}H^{2n-1}\\ O\\ OH\end{array}\right. + H^2.$$

Normal acrylic acid. Acetic acid. Homologue of acetic acid.

The formulæ of the individual acids are as follows:—

$$\begin{array}{ccccccccc} C^2\left\{\begin{array}{l} H \\ CH^2 \\ \hline O \\ OH \end{array}\right. & & C^2\left\{\begin{array}{l} H \\ C^2H^4 \\ \hline O \\ OH \end{array}\right. & & C^2\left\{\begin{array}{l} H \\ C^3H^6 \\ \hline O \\ OH \end{array}\right. & & C^2\left\{\begin{array}{l} H \\ C^4H^8 \\ \hline O \\ OH \end{array}\right. & \ldots\ldots & C^2\left\{\begin{array}{l} H \\ C^{16}H^{32} \\ \hline O \\ OH \end{array}\right. \\ \text{Acrylic.} & & \text{Crotonic.} & & \text{Angelic.} & & \text{Pyroterebic.} & & \text{Oleic.} \end{array}$$

It is easily seen from these formulæ that crotonic acid, when decomposed by an alkali, must yield two molecules of acetic acid, and that the other acids above represented must yield acetic acid, together with formic, propionic, butyric, and palmetic acids respectively.

3. **Acids of the Series** $C^nH^{2n-4}O^2$.—Of this series only three acids are known, viz. sorbic and parasorbic acids, $C^6H^8O^2$ (v. 352), and camphic acid, $C^{10}H^{16}O^2$ (i. 725).

4. Of the series $C^nH^{2n-6}O^2$ only one acid has yet been obtained, viz. *hydrobenzoic* or benzoleic acid, $C^7H^{10}O^2 = C^7H^9O(OH)$, formed, together with other products, by the action of water and sodium-amalgam on benzoic acid: $C^7H^6O^2 + 2H^2 = C^7H^{10}O^2$ (Hermann, *Ann. Ch, Pharm.* cxxxii. 75).

5. **Aromatic Series.** $C^nH^{2n-8}O^2$.—These acids are related to the aromatic hydrocarbons C^nH^{2n-6} in the same manner as the fatty acids to the paraffins. Benzoic acid, $C^7H^6O^2$, the lowest member of the series, may be derived from benzene, C^6H^6, by the substitution of carboxyl, (CO^2H), for an atom of hydrogen, its rational formula being $C^6H^5.CO^2H$. All the higher acids of the series exhibit isomeric modifications. Thus from toluene, C^7H^8, which has the composition of methylic benzene or phenyl-methyl, $C^6H^5.CH^3$ (v. 852), are derived normal toluic acid, $C^6H^4(CH^3).CO^2H$, the true homologue of benzoic acid, and alpha-toluic acid, $C^6H^5.CH^2CO^2H$, derived from toluene by substitution of carboxyl for an atom of hydrogen in the methyl atom. The known acids of the group are:

Benzoic	$C^7H^6O^2$	$= C^6H^5.CO^2H$	
Toluic	$C^8H^8O^2$	$= C^6H^4(CH^3).CO^2H$.	. α-Toluic $C^6H^5.CH^2CO^2H$
Xylic	$C^9H^{10}O^2$	$= C^6H^3(CH^3)^2.CO^2H$.	. α-Xylic $C^6H^4(CH^3).CH^2CO^2H$
Cumic	$C^{10}H^{12}O^2$	$= C^6H^4(C^3H^7).CO^2H$?	. α-Cymic $C^6H^3(CH^3)^2.CH^2CO^2H$?

The 9-carbon acid admits of another modification, viz. $C^6H^4(C^2H^5).CO^2H$, derived from ethyl-benzene, $C^6H^5(C^2H^5)$, isomeric with xylene, but it has not yet been obtained. The higher acids of the series are susceptible of a still larger number of modifications.

The aromatic acids may be formed synthetically from carbon dioxide by a process analogous to that already described in the case of the fatty acids (i. 61, 3°); e.g. benzoic acid by passing the gas into monobromobenzene containing sodium (Kekulé):

$$CO^2 + C^6H^5Br + Na^2 = NaBr + C^7H^5NaO^2.$$

See Toluic Acid (v. 861). For other modes of formation of these acids, see Aromatic Series.

6. **Acids of the Series** $C^nH^{2n-10}O^2$.—The acids of this series are related to the aromatic acids in the same manner as those of the acrylic series to the fatty acids. Only two of them are however at present known, viz. cinnamic acid and atropic acid, both containing $C^9H^8O^2$.

Cinnamic acid, described in vol. i. p. 983, as a product of the oxidation of cinnamic aldehyde, and by heating benzoic aldehyde with acetic chloride, is likewise formed synthetically, by the action of chorethylidene (produced by the action of carbonyl chloride on acetic aldehyde) on potassium benzoate:

$$\underset{\text{Aldehyde.}}{C^2H^4O} + \underset{\substack{\text{Carbonyl}\\\text{choride.}}}{COCl^2} = HCl + CO^2 + \underset{\text{Chlorethylidene.}}{C^2H^3Cl}$$

$$\underset{\substack{\text{Chlorethyl-}\\\text{idene.}}}{C^2H^3Cl} + \underset{\substack{\text{Potassium}\\\text{benzoate.}}}{C^7H^5KO^2} = KCl + \underset{\substack{\text{Cinnamic}\\\text{acid.}}}{C^9H^8O^2}$$

Atropic acid is a crystalline acid obtained, together with tropine (v. 895), by the action of alkalis on atropine:

$$\underset{\text{Atropine.}}{C^{17}H^{23}NO^3} = \underset{\substack{\text{Atropic}\\\text{acid.}}}{C^9H^8O^2} + \underset{\text{Tropine.}}{C^8H^{15}NO}$$

DIATOMIC ACIDS.

These acids are derived from diatomic alcohols by substitution either of O for H^2, in which case they contain 3 at. of oxygen, and are monobasic, or by substitution of O^2 for H^4, in which case they contain 4 at. of oxygen, and are bibasic.

The relation between the saturated hydrocarbons, the glycols, and the diatomic acids is shown in the following table:

Hydrocarbons.	Glycols.	Diatomic Acids.	
		Monobasic.	Bibasic.
C^nH^{2n+2}	$C^nH^{2n+2}O^2$	$C^nH^{2n}O^3$	$C^nH^{2n-2}O^4$
C^nH^{2n}	$C^nH^{2n}O^2$	$C^7H^{2n-2}O^3$	$C^nH^{2n-4}O^4$
C^nH^{2n-2}	$C^nH^{2n-2}O^2$	$C^nH^{2n-4}O^3$	$C^nH^{2n-6}O^4$
C^nH^{2n-4}	$C^nH^{2n-4}O^2$	$C^nH^{2n-6}O^3$	$C^nH^{2n-8}O^4$.
	&c.	&c.	

Diatomic and Monobasic Acids.

1. **Lactic Series.** $C^nH^{2n}O^3$.—The acids of this series may be divided into two groups, distinguished as normal lactic acids and isolactic acids. The known members of the series are:

Glycollic or Oxyacetic acid, $C^2H^4O^3$.
Lactic or Oxypropionic acid, $C^3H^6O^3$.
Oxybutyric acid, $C^4H^8O^3$, and its isomeride, Dimethoxalic acid.
Oxyvaleric acid, $C^5H^{10}O^3$, and its isomeride, Ethomethoxalic acid.
Leucic or Oxycaproic acid, $C^6H^{12}O^3$, and its isomeride, Diethoxalic acid.

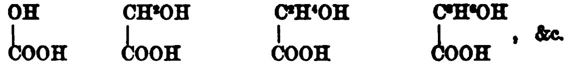
Acids homologous with dimethoxalic acid, and containing 7, 9, and 12 at. of carbon, have also been obtained.

The normal lactic acids correspond to the diatomic alcohols homologous with ethenic alcohol (glycol); thus:

$$\begin{array}{l} C^{n-1}H^{2n}\text{-}OH \\ | \\ CH^2OH \end{array} \qquad \begin{array}{l} C^{n\ 1}H^{2n-2}OH \\ | \\ COOH \end{array}$$

Diatomic acohol. Normal acid of lactic series.

If in the second formula we make n successively equal to 1, 2, 3, &c., we get the series:

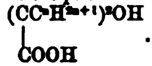


$$\begin{array}{l} OH \\ | \\ COOH \end{array} \quad \begin{array}{l} CH^2OH \\ | \\ COOH \end{array} \quad \begin{array}{l} C^2H^4OH \\ | \\ COOH \end{array} \quad \begin{array}{l} C^3H^6OH \\ | \\ COOH \end{array} \text{, \&c.}$$

Carbonic acid. Glycollic acid. Lactic acid. Oxybutyric acid.

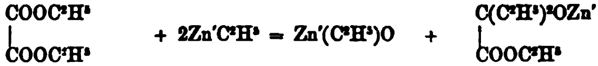
Carbonic acid is, however, a bibasic acid, for reasons already explained. The general modes of formation of the normal lactic acids are given in vol. i. p. 52.

The Isolactic acids are represented by the general formula,



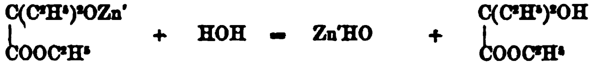
$$\begin{array}{l} (CC^nH^{2n+1})^2OH \\ | \\ COOH \end{array}.$$

They are obtained in the form of ethers by the action of the zinc-compound of an alcohol-radicle, C^nH^{2n+1}, on a neutral ether of oxalic acid containing a radicle of the same series, such as diethylic oxalate. The reaction consists in the replacement of an atom of oxygen in the oxalic ether by two equivalents of alcohol-radicle, and the simultaneous replacement of an equivalent of ethyl, methyl, &c., in the oxalic ether by any equivalent * of zinc, whereby an ether of zinc-diethyloxalic acid, &c., is produced, which by certain obvious transformations may be converted into the required acid; thus:



$$\begin{array}{l} COOC^2H^5 \\ | \\ COOC^2H^5 \end{array} + 2Zn'C^2H^5 = Zn'(C^2H^5)O + \begin{array}{l} C(C^2H^5)^2OZn' \\ | \\ COOC^2H^5 \end{array}$$

Dimethylic oxalate. Zinc ethide. Zinc ethylate. Ethylic zinco-diethoxalate.



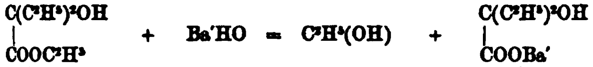
$$\begin{array}{l} C(C^2H^5)^2OZn' \\ | \\ COOC^2H^5 \end{array} + HOH = Zn'HO + \begin{array}{l} C(C^2H^5)^2OH \\ | \\ COOC^2H^5 \end{array}$$

Ethylic-zinco-diethoxalate. Water. Zinc hydrate. Ethylic diethoxalate.

---

* To simplify the equations, the *equivalent* of zinc (Zn' = 32·5) is used instead of the atom

The ethylic diethoxalate is easily decomposed by baryta-water, yielding ethyl alcohol and barium diethoxalate:



$$\underset{\substack{\text{Ethylic}\\ \text{diethoxalate.}}}{\begin{array}{l}C(C^2H^5)^2OH\\ |\\ COOC^2H^5\end{array}} + Ba'HO = C^2H^5(OH) + \underset{\substack{\text{Barium}\\ \text{diethoxalate.}}}{\begin{array}{l}C(C^2H^5)^2OH\\ |\\ COOBa'\end{array}}$$

And this salt decomposed by sulphuric acid yields diethoxalic acid, $\left\{\begin{array}{l}C(C^2H^5)^2OH\\ |\\ COOH\end{array}\right.$, isomeric with leucic acid.

In the first stage of the process it is found best to use a mixture of ethyl iodide with metallic zinc, which produces zinc-ethide, instead of the latter compound previously prepared. The other isolactic ethers are prepared in a similar manner.

The isolactic acids are described under Oxalic Ethers (iv. 275).

The acids of either group are reduced by hydriodic acid to the corresponding acids of the acetic series; e.g.,

$$\underset{\substack{\text{Lactic}\\ \text{acid.}}}{C^3H^6O^3} + 2HI = \underset{\substack{\text{Propionic}\\ \text{acid.}}}{C^3H^6O^2} + H^2O + I^2.$$

The ethereal salts of the isolactic acids are converted by phosphorus trichloride or pentoxide into ethers of the iso-acrylic acids (p. 41); the ethereal salts of the normal lactic acids do not exhibit this reaction.

The normal lactic acids, when heated, give up a molecule of water, and are converted into oxygen-ethers or anhydrides; e.g., $C^3H^6O^3$ (lactic acid) $-$ H^2O $=$ $C^3H^4O^2$ (lactide). Two molecules of a normal lactic acid may also be deprived of a molecule of water, thereby producing a condensed acid, analogous to the polyethylenic alcohols; e.g., $2C^3H^6O^3$ (lactic acid) $-$ H^2O $=$ $C^6H^{10}O^5$ (dilactic acid).

Both the normal and the isolactic acids undergo a characteristic and perfectly definite oxidation by weak solutions of chromic acid, yielding carbon dioxide, water, and an aldehyde or a ketone; thus:

$$\underset{\text{Diethoxalic acid.}}{C(C^2H^5)^2OH.COOH} + O = CO^2 + H^2O + \underset{\text{Propione.}}{CO(C^2H^5)^2}$$

$$\underset{\text{Lactic acid.}}{C(CH^3)HOH.COOH} + O = CO^2 + H^2O + \underset{\text{Aldehyde.}}{CO(CH^3)H}$$

2. **Pyruvic Series.** $C^nH^{2n-2}O^3$.—This is a small group of acids including pyruvic acid, $C^3H^4O^3$; convolvulinoleic acid, $C^{13}H^{24}O^3$?; jalapinoleic acid, $C^{16}H^{30}O^3$?; ricinoleic acid, $C^{18}H^{34}O^3$. These acids are described in the Dictionary in their alphabetical places. There are no general modes of formation or decomposition to be noticed respecting them.

3. **Series** $C^nH^{2n-4}O^3$.—The only known acid of this series is guiacic acid, $C^6H^8O^3$, a crystallisable substance obtained from guaiacum (ii. 948).

4. **Series** $C^nH^{2n-8}O^3$.—This series includes the following acids, related to the monatomic aromatic acids in the same manner as the lactic acids to the fatty acids:—

Oxybenzoic, Paraoxybenzoic, and Salicylic acids	$C^7H^6O^3$
Formobenzoic, Cresotic, Carbocresylic, and Anisic acids	$C^8H^8O^3$
Phloretic and Isophloretic, Hydrocoumaric or Melilotic, and Hydroparacoumaric acids	$C^9H^{10}O^3$.
Thymotic and Thymylcarbonic acids	$C^{11}H^{14}O^3$.

Oxybenzoic, para-oxybenzoic and salicylic acids have the constitution represented by the formula $C^6H^4(OH).CO^2H$, the differences of chemical character which they exhibit depending most probably upon the different relative positions of the groups OH and CO^2H which they contain. (See Aromatic Series.) They are all resolved by heat, but with various degrees of facility, into carbon dioxide and phenol, salicylic acid undergoing this decomposition easily, and paraoxybenzoic acid still more easily, whereas oxybenzoic acid sublimes undecomposed when slowly heated, and splits up in the manner just mentioned only when quickly heated (iv. 295). Oxybenzoic acid is produced by the action of nitrous acid on amidobenzoic acid:

$$C^6H^4(NH^2).CO^2H + NO(OH) = C^6H^4(OH).CO^2H + H^2O + N^2;$$

paraoxybenzoic acid, by heating anisic (methyl-paraoxybenzoic acid) with hydriodic acid:

$$C^7H^5(CH^3)O^3 + HI = CH^3I + C^7H^6O^3;$$

and salicylic acid, by passing carbon dioxide into phenol containing small quantities of sodium:

$$\underset{\substack{\text{Sodium}\\\text{phenate.}}}{C^6H^5ONa} + CO^2 = \underset{\substack{\text{Sodium}\\\text{salicylate.}}}{C^7H^5O^3Na}$$

Carbocresylic and **Cresotic acids**, $C^8H^8O^3$, are produced simultaneously by the action of carbon dioxide and sodium on cresol, just as salicylic acid is produced from phenol. Both these acids may be regarded as hydroxyl-derivatives of normal toluic acid:

$C^6H^4(CH^3).COOH$ . . . . . Toluic acid.
$C^6H^3(OH)(CH^3).COOH$ . . . . Carbocresylic and Cresotic acids.

With regard to facility of resolution into carbon dioxide and cresol, carbocresylic acid appears to be related to cresotic acid, in the same manner as salicylic to oxybenzoic acid (ii. 106).

Formobenzoic or **Mandelic acid** (iii. 800) is related to α-toluic acid in the same manner as the two preceding acids to normal toluic acid:

$C^6H^5.CH^2COOH$ . . . . α-toluic acid.
$C^6H^5.CH(OH)COOH$ . . . . Formobenzoic acid.

It is produced by the action of hydrochloric acid on crude bitter almond oil (containing hydrocyanic acid).

Anisic acid is shown to have the composition of **methyl-paraoxybenzoic acid** by the fact that it may be produced by treating the potassium salt of paraoxybenzoic acid with methyl-iodide:

$$\underset{\substack{\text{Potassium}\\\text{paraoxybenzoate.}}}{C^7H^4K^2O^3} + 2CH^3I = 2KI + \underset{\substack{\text{Methylic methyl-}\\\text{paraoxybenzoate.}}}{C^7H^4(CH^3)O^3.CH^3}$$

$$\underset{\substack{\text{Methylic methyl-}\\\text{paraoxybenzoate.}}}{C^7H^4(CH^3)O^3.CH^3} + H^2O = CH^3(OH) + \underset{\substack{\text{Methyl-paraoxy-}\\\text{benzoic or anisic acid.}}}{C^7H^5(CH^3)O^3.}$$

Methyl-salicylic and **phenyl-glycollic acid**, $C^2H^3(C^6H^5)O^3$, are likewise isomeric with the acids of this group.

Ethyl-paraoxybenzoic acid, $C^7H^5(C^2H^5)O^3$, may be prepared in like manner by the action of ethyl-iodide on paraoxybenzoic acid. This acid is identical with hydroparacoumaric acid, and isomeric with hydrocoumaric, phloretic, and isophloretic acids.

Another acid, isomeric with the preceding, is produced by the action of alkalis on the cyanhydrin of anisic alcchol:

$$\underset{\substack{\text{Anisic}\\\text{cyanhydrin.}}}{C^8H^8(OH)CN} + 2H^2O = NH^3 + \underset{\text{Acid.}}{C^8H^8(OH).CO^2H}$$

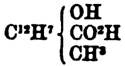
Thymyl-carbonic and **Thymotic acids**, $C^{11}H^{14}O^3$, homologous with carbocresylic and cresotic acids respectively, are produced by the action of carbon dioxide and sodium on thymel (v. 794).

5. **Series** $C^nH^{2n-10}O^3$.—To this series belongs **coumaric acid**, $C^9H^8O^3$, produced by the action of boiling potash on coumarin. Homologues of this acid, called *butyric coumaric acid*, $C^{11}H^{12}O^3$, and *valeric coumaric acid*, $C^{12}H^{14}O^3$, have lately been obtained by a synthetical process (Perkin, *Chem. Soc. J.* [2] vi. 475). (See COUMARIC ACID and COUMARIN.)

6. There are no known acids belonging to the series $C^nH^{2n-12}O^3$ and $C^nH^{2n-14}O^3$.

7. Of the series $C^nH^{2n-16}O^3$ the only known member is **benzilic acid**, $C^{14}H^{12}O^3$, produced by the action of alcoholic potash on benzoin (i. 546). It may be regarded as a derivative of diphenyl; thus:

$$\underset{\text{Diphenyl.}}{C^{12}H^{10}}$$



$$C^{12}H^7\left\{\begin{matrix}OH\\CO^2H\\CH^3\end{matrix}\right.$$

Benzilic acid

Diatomic and Bibasic Acids.

These acids contain the group carboxyl twice, and therefore 4 atoms of oxygen. They may all be included in the general formula $R''(CO^2H)^2$, where R denotes a diatomic hydrocarbon-radicle; or they may be regarded as compounds of oxygenated diatomic radicles with two equivalents of hydroxyl; e.g. succinic acid, $(C^4H^4O^2)''(OH)^2$.

The known acids of this group belong to the series $C^nH^{2n-2}O^4$, $C^nH^{2n-4}O^4$, $C^nH^{2n-6}O^4$, and $C^nH^{2n-10}O^4$. The acids of the first series, and probably also those of the third and fourth, are saturated compounds; but those of the second are unsaturated, being capable of taking up two atoms of hydrogen, bromine, and other monad elements, whereby they are converted into acids of the first series.

1.—**Oxalic or Succinic Series,** $C^nH^{2n-2}O^4$.

The known acids of this series are:

Oxalic acid	$C^2H^2O^4$	Pimelic acid	$C^7H^{12}O^4$
Malonic acid	$C^3H^4O^4$	Suberic acid	$C^8H^{14}O^4$
Succinic acid	$C^4H^6O^4$	Anchoic acid	$C^9H^{16}O^4$
Pyrotartaric acid	$C^5H^8O^4$	Sebic acid	$C^{10}H^{18}O^4$
Adipic acid	$C^6H^{10}O^4$	Roccellic acid	$C^{17}H^{32}O^4$

They are produced: α. By oxidation of the corresponding glycols, $R''(CH^2OH)^2$, the change consisting in the substitution of O^2 for H^4 (p. 44). In this manner oxalic acid, $C^2H^2O^4$, is formed from ethylene alcohol, $C^2H^6O^2$, and malonic acid, $C^3H^4O^4$, from propylene alcohol, $C^3H^8O^2$; but the higher glycols split up under the influence of oxidising agents, and do not yield bibasic acids containing the same number of carbon-atoms as themselves.

β. By boiling the cyanides of diatomic alcohol-radicles with alcoholic potash; e.g.,

$$\underset{\substack{\text{Propylene}\\\text{cyanide.}}}{(C^3H^6)''(CN)^2} + 2KOH + 2H^2O = 2NH^3 + \underset{\substack{\text{Potassium}\\\text{pyrotartrate.}}}{(C^3H^6)''(CO^2K)^2}$$

This reaction is analogous to that by which the fatty acids are formed from the cyanides of the monatomic alcohol-radicles, C^nH^{2n+1}.

γ. By the addition of hydrogen to other acids containing a smaller proportion of that element; in this manner succinic acid, $C^4H^6O^4$, is formed from fumaric acid, $C^4H^4O^4$.

δ. By the action of heat on acids of more complicated structure; e.g.,

$$\underset{\substack{\text{Tartaric}\\\text{acid.}}}{2C^4H^6O^6} = 3CO^2 + 2H^2O + \underset{\substack{\text{Pyrotartaric}\\\text{acid.}}}{C^5H^8O^4}.$$

ε. Many of these acids are produced by the action of powerful oxidisers on a variety of organic bodies: thus, succinic acid, $C^4H^6O^4$, and its homologues, are produced by treating various fatty and resinous bodies with nitric acid.

2. **Fumaric Series.** $C^nH^{2n-4}O^4$.—This series includes the two following groups of isomeric acids:

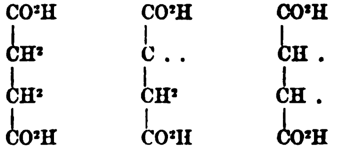
Fumaric and Maleic acids	$C^4H^4O^4$
Itaconic, Citraconic, and Mesaconic acids	$C^5H^6O^4$

They are for the most part unsaturated compounds, capable of taking up two atoms of hydrogen, bromine, or other monad elements, or a molecule of a hydracid, such as HCl or HBr, and passing into acids of the preceding series. Thus itaconic acid, $C^5H^6O^4$, treated with sodium amalgam is converted into pyrotartaric acid, $C^5H^8O^4$; fumaric acid, $C^4H^4O^4$, treated with bromine yields dibromo-succinic acid, $C^4H^4Br^2O^4$; and citraconic acid treated with hydrochloric acid is converted into citramonochloropyrotartaric acid, $C^5H^7ClO^4$.

The fixation of a molecule of hydrogen converts the several isomeric non-saturated acids into one and the same saturated acid: thus the three pyrocitric acids, $C^5H^6O^4$, are all converted in this way into pyrotartaric acid. But the fixation of bromine gives rise to brominated acids which are not identical, but isomeric, like the unsaturated acids from which they are formed; on replacing the bromine with hydrogen, however, these several brominated acids yield the same saturated acid.

Kekulé, who discovered these facts, explains them as follows (*Ann. Ch. Pharm. Suppl.* ii. 111; further, *Bulletin de l'Académie royale de Belgique* [2] xxiv. 25; *Laboratory*, p. 370).

Maleic and fumaric acids may be regarded as derived from the saturated compound succinic acid, by the loss of 2 atoms of hydrogen; but in the case of maleic acid it may be supposed that the two hydrogen atoms thus removed belonged to the same atom of carbon; in that of fumaric acid, to different atoms of carbon; thus:

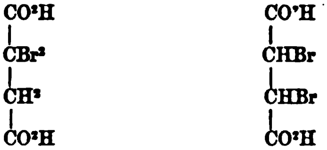


$$\begin{array}{lll} CO^2H & CO^2H & CO^2H \\ | & | & | \\ CH^2 & C\,.\,. & CH\,. \\ | & | & | \\ CH^2 & CH^2 & CH\,. \\ | & | & | \\ CO^2H & CO^2H & CO^2H \end{array}$$

Succinic. Maleic. Fumaric.

The dots in these formulæ represent the gaps left by the removal of the hydrogen atoms, or, in other words, the unsaturated atomicities or equivalencies of the carbon-atoms.

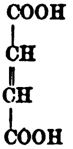
Now it is clear that the addition of H^2 to either of these unsaturated molecules must yield the same product, viz. succinic acid, but that the addition of 2 atoms of bromine to the first or to the second will yield different products, viz.:



$$\begin{array}{ll} CO^2H & CO^2H \\ | & | \\ CBr^2 & CHBr \\ | & | \\ CH^2 & CHBr \\ | & | \\ CO^2H & CO^2H \end{array}$$

Maleo-dibromosuccinic. Fumaro-dibromosuccinic.

Fumaric acid is, however, a much more stable compound than maleic acid, and less inclined to take up hydrogen or bromine than maleic acid: hence it is probable that the two middle atoms of carbon in the former are united more intimately than in the latter, and that it is really a saturated compound represented by the formula:

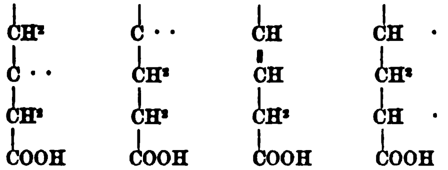


$$\begin{array}{l} COOH \\ | \\ CH \\ \| \\ CH \\ | \\ COOH \end{array}$$

Fumaric acid.

A body so constituted will not take up a molecule of bromine till the connection between the carbon-atoms has been somewhat loosened by the action of that element; whereas maleic acid, which is an unsaturated compound, can take up the bromine immediately, to form dibromosuccinic acid.

The isomeric acids, $C^5H^6O^4$, may in like manner be represented by the following formulæ:

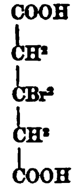


$$\begin{array}{llll} COOH & COOH & COOH & COOH \\ | & | & | & | \\ CH^2 & C\cdot\cdot & CH & CH\;\cdot \\ | & | & \| & | \\ C\cdot\cdot & CH^2 & CH & CH^2 \\ | & | & | & | \\ CH^2 & CH^2 & CH^2 & CH\;\cdot \\ | & | & | & | \\ COOH & COOH & COOH & COOH \end{array}$$

Itaconic. Citraconic. Mesaconic. Unknown isomeride.

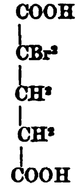
The first three of these acids, when treated with bromine, take up two atoms of that element, and form dibromopyrotartaric acid, $C^5H^6Br^2O^2$; but mesaconic acid takes up bromine and hydrogen much less readily than itaconic or citraconic acid, being in fact related to these acids in the same way as fumaric to maleic acid.

The three modifications of dibromopyrotartaric acid are represented by the formulæ:



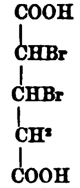
$$\begin{array}{l}COOH\\|\\CH^2\\|\\CBr^2\\|\\CH^2\\|\\COOH\end{array}$$

Itadibromo-pyrotartaric.



$$\begin{array}{l}COOH\\|\\CBr^2\\|\\CH^2\\|\\CH^2\\|\\COOH\end{array}$$

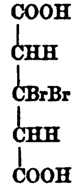
Citradibromo-pyrotartaric.



$$\begin{array}{l}COOH\\|\\CHBr\\|\\CHBr\\|\\CH^2\\|\\COOH\end{array}$$

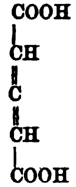
Mesadibromo-pyrotartaric.

Itadibromopyrotartaric acid treated with alkalis gives rise to aconic acid, $C^5H^4O^4$, the two atoms of bromine uniting with two atoms of hydrogen, and two molecules of hydrobromic acid being eliminated, while the three carbon-atoms forming the centre of the molecule unite together in a more intimate manner; thus:



$$\begin{array}{l}COOH\\|\\CHH\\|\\CBrBr\\|\\CHH\\|\\COOH\end{array}$$

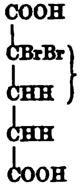
Itadibromopyrotartaric acid.



$$\begin{array}{l}COOH\\|\\CH\\\|\\C\\\|\\CH\\|\\COOH\end{array}$$

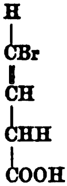
Aconic acid.

The two other modifications of dibromopyrotartaric acid when similarly treated both yield monobromocrotonic acid, $C^4H^5BrO^2$. These reactions are explained by the following formulæ, in which the elements removed in the form of hydrobromic acid are indicated by brackets:



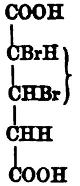
$$\begin{array}{l}COOH\\|\\\left.\begin{array}{l}CBrBr\\|\\CHH\end{array}\right\}\\|\\CHH\\|\\COOH\end{array}$$

Citradibromo-pyrotartaric.



$$\begin{array}{l}H\\|\\CBr\\\|\\CH\\|\\CHH\\|\\COOH\end{array}$$

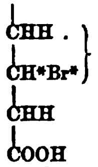
Monobromo-crotonic.



$$\begin{array}{l}COOH\\|\\\left.\begin{array}{l}CBrH\\|\\CHBr\end{array}\right\}\\|\\CHH\\|\\COOH\end{array}$$

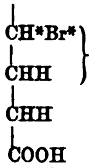
Mesadibromo-pyrotartaric.

Another reaction, easily explained by these formulæ, is the conversion of itaconic and citraconic acids into mesaconic acid by the action of hydrobromic acid. The gaps in the molecule are first filled up, and then hydrobromic acid is eliminated; but to produce this acid the bromine takes up an atom of hydrogen different from that with which it entered. This reaction is represented by the following formulæ, in which the elements of the hydrobromic acid which go out are indicated by a brace, those of the hydrobromic acid which enters, by asterisks; these latter correspond to the gaps in the generating acids:



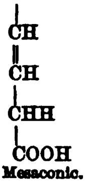
$$\begin{array}{l}COOH\\|\\\left.\begin{array}{l}CHH\ .\\|\\CH{*}Br{*}\end{array}\right\}\\|\\CHH\\|\\COOH\end{array}$$

Itamonobromo-pyrotartaric.



$$\begin{array}{l}COOH\\|\\\left.\begin{array}{l}CH{*}Br{*}\\|\\CHH\end{array}\right\}\\|\\CHH\\|\\COOH\end{array}$$

Citramonobromo-pyrotartaric.



$$\begin{array}{l}COOH\\|\\CH\\\|\\CH\\|\\CHH\\|\\COOH\end{array}$$

Mesaconic.

This transformation of itaconic and citraconic acids into mesaconic acid shows further that mesaconic acid must be represented by the third and not by the fourth of the formulæ above given (p. 48). An acid having the constitution represented by this last formula might indeed be formed from citraconic, but not from itaconic acid.

Itamonochloropyrotartaric acid, $C^5H^7ClO^4$, boiled with water gives up hydrochloric acid, and yields an acid called paraconic acid, having the same composition as itaconic acid, &c., but monobasic (Swarts, *Bull. Acad. Belg.* [2] xxiv. 25). (See PYROCITRIC ACIDS, under CITRIC ACID.)

Camphoric acid, $C^{10}H^{16}O^4$, is likewise a bibasic acid included in the general formula $C^nH^{2n-4}O^2$. It appears to be a saturated compound, inasmuch as its ethylic ether shows no tendency to take up chlorine or other monatomic elements.

3. **Series** $C^nH^{2n-6}O^4$.—Aconic acid, $C^5H^4O^4$, produced by treating itadibromopyrotartaric acid with excess of caustic alkali, is comprised in this formula, but it appears to be monobasic.

4. **Series** $C^nH^{2n-8}O^4$.—The only bibasic acid represented by this formula is quinoylic or quinonic acid, $C^6H^4O^4$, which moreover is known only in its dichlorinated derivative, $C^6H^4Cl^2O^4$ (v. 34).

5. **Series** $C^nH^{2n-10}O^4$.—This series includes the isomeric acids, phthalic, isophthalic, and terephthalic, $C^8H^6O^4$ or $C^6H^4.(CO^2H)^2$, the isomerism of which appears to depend upon the relative positions of the two atoms of carboxyl, CO^2H. (See AROMATIC SERIES.)

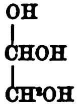
TRIATOMIC ACIDS.

These acids are derived from triatomic alcohols, by substitution of 1, 2 or 3 at. oxygen for 1, 2 or 3 molecules of hydrogen, and are accordingly either monobasic acids containing 4 at. oxygen, bibasic acids containing 5 at. oxygen, or tribasic acids containing 6 at. oxygen.

Triatomic and *Monobasic Acids.*—There are only three acids that can with certainty be referred to this group, viz.,

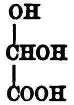
Glyoxylic acid . . . . $C^2H^4O^4$.
Glyceric acid . . . . $C^3H^6O^4$.
Oxysalicylic acid . . . . $C^7H^6O^4$.

Glyoxylic acid may be regarded as a derivative of the unknown ethenyl alcohol, $(C^2H^3)'''(HO)^3$, thus:



$$\begin{array}{l} OH \\ | \\ CHOH \\ | \\ CH^2OH \end{array}$$

Ethenyl alcohol.



$$\begin{array}{l} OH \\ | \\ CHOH \\ | \\ COOH \end{array}$$

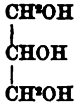
Glyoxylic acid.

Its composition is indicated by its formation from oxalic acid by the action of nascent hydrogen: $C^2H^2O^4 + H^2 = C^2H^4O^4$, and from bromoglycollic acid by boiling the silver-salt of that acid with water:

$$C^2H^2AgBrO^2 + H^2O = AgBr + C^2H^4O^4.$$

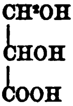
For the further discussion of its formula see GLYOXYLIC ACID.

Glyceric acid, $C^3H^6O^4$ (ii. 875), is derived in like manner from propenyl alcohol or glycerin $(C^3H^5)'''(OH)^3$.



$$\begin{array}{l} CH^2OH \\ | \\ CHOH \\ | \\ CH^2OH \end{array}$$

Glycerin.



$$\begin{array}{l} CH^2OH \\ | \\ CHOH \\ | \\ COOH \end{array}$$

Glyceric acid.

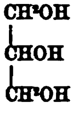
Oxysalicylic acid, $C^7H^6O^4$, which may be regarded as salicylic acid having 1 at. H replaced by HO, is produced by the action of boiling potash on mono-iodosalicylic acid:

$$C^7H^5IO^3 + KHO = KI + C^7H^5(HO)O^3.$$

It is isomeric with carbo-hydroquinonic, hypogallic and protocatechuic acids, all of which are likewise monobasic.

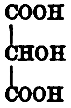
There are a few other monobasic acids containing 4 at. oxygen, which probably also belong to this group, viz. eugetic acid, $C^{11}H^{12}O^4$, produced by the action of carbon dioxide and sodium on eugenol or eugenic acid (oxidised essence of cloves), just as salicylic acid is produced from phenol; orsellinic acid, $C^8H^8O^4$, everninic acid, $C^9H^{10}O^4$, and parellic acid, $C^9H^6O^4$, produced by the action of alkalis on the colouring principles of certain lichens (ii. 611; iv. 235, 355); and piperic acid, $C^{12}H^{10}O^4$, produced by boiling piperine with potash.

Triatomic and Bibasic Acids.—The only known acids of this group are tartronic acid, $C^3H^4O^5$, malic acid, $C^4H^6O^5$, itamalic acid, $C^5H^8O^5$, and perhaps also croconic acid, $C^5H^2O^5$. The alcohols corresponding to these acids are not known, neither have any general methods of forming the acids been discovered. The relations of tartronic and malic acids to their respective unknown alcohols, $C^3H^8O^3$ and $C^4H^{10}O^3$, are shown by the following formulæ:



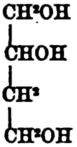
$$\begin{array}{l}CH^2OH\\ |\\ CHOH\\ |\\ CH^2OH\end{array}$$

Unknown alcohol.



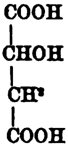
$$\begin{array}{l}COOH\\ |\\ CHOH\\ |\\ COOH\end{array}$$

Tartronic acid.



$$\begin{array}{l}CH^2OH\\ |\\ CHOH\\ |\\ CH^2\\ |\\ CH^2OH\end{array}$$

Unknown alcohol.



$$\begin{array}{l}COOH\\ |\\ CHOH\\ |\\ CH^2\\ |\\ COOH\end{array}$$

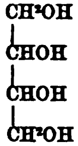
Malic acid.

Itamalic acid, lately discovered by Swarts, is formed by the action of water or alkalis on itachloropyrotartaric acid, $C^5H^7ClO^4 + H^2O = C^5H^8O^5 + HCl$.

Triatomic and Tribasic Acids.—But few of these acids have been obtained; indeed, the only ones known with certainty to belong to the group are aconitic acid, $C^6H^6O^6 = (C^3H^3)'''.(CO^2H)^3$, and tricarballylic acid, $C^6H^8O^6 = (C^3H^5)'''(CO^2H)^3$, which is produced by the action of alkalis on propenyl tricyanide or tricyanhydrin (v. 879).

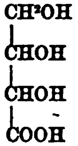
TETRATOMIC ACIDS.

These acids may be derived from tetratomic alcohols by substitution of 1, 2, 3 and 4 atoms of oxygen for a corresponding number of hydrogen molecules; thus:



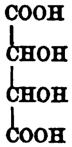
$$\begin{array}{l}CH^2OH\\ |\\ CHOH\\ |\\ CHOH\\ |\\ CH^2OH\end{array}$$

Erythrite.



$$\begin{array}{l}CH^2OH\\ |\\ CHOH\\ |\\ CHOH\\ |\\ COOH\end{array}$$

Erythric acid (monobasic).



$$\begin{array}{l}COOH\\ |\\ CHOH\\ |\\ CHOH\\ |\\ COOH\end{array}$$

Tartaric acid (bibasic).

Only one tetratomic acid has, however, been actually formed by oxidation of the corresponding alcohol, viz. erythric acid, $C^4H^8O^5$, from erythrite, $C^4H^{10}O^4$. The known tetratomic acids are:

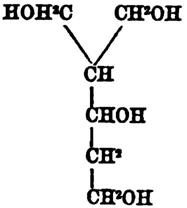
Erythric acid	$C^4H^8O^5$	monobasic.
Gallic acid	$C^7H^6O^5$	
Tartaric acid	$C^4H^6O^6$	bibasic.
Homotartaric acid	$C^5H^8O^6$	
Citric acid	$C^6H^8O^7$	tribasic.

Homotartaric acid is produced by the action of moist silver oxide on dibromopyrotartaric acid:

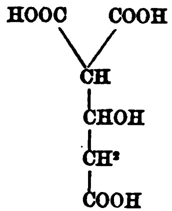
$$C^5H^6Br^2O^4 + Ag^2O + H^2O = 2AgBr + C^5H^8O^6.$$

Rhodizonic acid, $C^6H^4O^6$, obtained by heating with alcohol the black mass resulting from the action of carbon monoxide on heated potassium, is also a bibasic acid containing 6 at. oxygen.

Citric acid is a tribasic acid, $C^6H^8O^7 = (C^3H^4O)'''(COOH)^3$, which may be derived from the unknown tetratomic alcohol, $C^6H^{14}O^4$.



Tetratomic alcohol.



Citric acid.

Meconic acid, $C^7H^4O^7$, obtained from opium, is also a tribasic acid, but its degree of atomicity has not yet been determined.

PENTATOMIC ACIDS.

There is but one known acid that can be referred to this group, viz. **quinic** or **kinic** acid, $C^7H^{12}O^6$ (v. 9), which is monobasic, and may perhaps be represented by the formula $(C^6H^7)^v\left\{\begin{matrix}(OH)^4\\ CO^2H\end{matrix}\right.$.

HEXATOMIC ACIDS.

Four acids of this class are known, viz. **mannitic acid**, $C^6H^{12}O^7$, the isomeric acids, **saccharic** and **mucic**, $C^6H^{10}O^8$, all of which appear to be bibasic, and **mellitic acid**, $C^{12}H^6O^{12}$ which is sexbasic. The first three of these acids are derived from the hexatomic alcohol, mannite, $C^6H^{14}O^6$, in the manner indicated by the following formulæ:

$$\begin{array}{ccc}
CH^2OH & CH^2OH & COOH \\
| & | & | \\
CHOH & CHOH & CHOH \\
| & | & | \\
CHOH & CHOH & CHOH \\
| & | & | \\
CHOH & CHOH & CHOH \\
| & | & | \\
CHOH & CHOH & CHOH \\
| & | & | \\
CH^2OH & COOH & COOH \\
\text{Mannite.} & \text{Mannitic acid.} & \text{Saccharic acid.}
\end{array}$$

The bibasicity of mannitic acid seems to show that the influence of the oxygen on the group COOH, in facilitating the exchange of the typic hydrogen for a metal may extend to the group CHOH, which is next to it.

Mannite is actually converted into mannitic acid by oxidation under the influence of platinum-black, and into saccharic acid by the action of nitric acid.

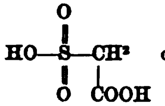
Mellitic acid, formerly regarded as a bibasic acid and represented by the formula $C^4H^2O^4$ (iii. 870), appears from the recent researches of Baeyer (*Ann. Ch. Pharm.* cxli. 271) to be a hexatomic and sexbasic acid, $C^6(CO^2H)^6$, derived from benzene, C^6H^6, by substitution of 6 equivalents of carboxyl, CO^2H, for 6 at. hydrogen. It therefore belongs to the aromatic series. When heated with lime it is completely resolved into carbonic acid and benzene, $C^6(CO^2H)^6 + 6CaO = C^6H^6 + 6CO^3Ca$. When treated with sodium amalgam it takes up 6 at. H, and is converted into the sexbasic acid $C^6H^6(CO^2H)^6$; and this when treated with sulphuric acid is converted into the tetrabasic acid $C^6H^2(CO^2H)^4$.

* * *

The preceding groups include all the organic acids containing only carbon, hydrogen and oxygen whose chemical relations have been exactly investigated; but it need scarcely be added that there is still a considerable number, especially those existing in living organisms, whose places in the series cannot at present be determined.

Most organic acids when subjected to the action of *chlorine* or *bromine* give up one or more atoms of hydrogen in exchange for chlorine or bromine. **Iodated acids** are formed in like manner, sometimes by the action of *iodine*, sometimes by that of *chloride of iodine*. **Nitrated acids**, in which one or more equivalents of nitryl, NO^2, are substituted for hydrogen, are formed by subjecting organic acids to the action of strong *nitric acid*. All these substitutions take place within the radicle of the acid, and do not affect its basicity. Another important class of acids is constituted by the **amic** or **amidated acids**, formed by dehydration of acid ammonium salts, by the action of hydrogen sulphide or other reducing agents on nitrated acids, and by the action of ammonia on acid ethers, e.g. oxamic acid from acid ethylic oxalate.

Sulpho-acids. There is also a peculiar class of acids containing **sulphur**, formed by the action of fuming sulphuric acid or sulphuric anhydride on hydrocarbons, alcohols, acids and amides. They contain the elements of a hydrocarbon, an alcohol, or an acid, combined with one or two molecules of sulphuric anhydride, and may be regarded as derived from hydrocarbons, alcohols, and acids by substitution of the univalent radicle SO^3H for hydrogen. Those derived from acids also contain the radicle carboxyl, CO^2H. Thus **sulphacetic acid** formed by the action of sulphuric anhydride on glacial acetic acid has the composition $C^2H^4O^2.SO^3$, and its constitution may be represented by the following formulæ:



$$\begin{array}{c}\mathrm{O}\\ \|\\ \mathrm{HO{-}S{-}CH^2}\\ \|\quad|\\ \mathrm{O\ \ COOH}\end{array} \quad\text{or}\quad \begin{array}{c}\mathrm{C}\\ |\\ \mathrm{C}\end{array}\left\{\begin{array}{l}H^3\\ \underline{SO^3H}\\ O''\\ OH\end{array}\right. \quad\text{or}\quad CH^2(SO^3H).CO^2H.$$

In like manner, disulphometholic or methionic acid, $CH^4.2SO^3$, produced by the prolonged action of fuming sulphuric acid on sulphacetic acid, may be regarded as $CH^2(SO^3H)^2$, that is as marsh gas having 2 at. hydrogen replaced by the radicle SO^3H.

Both sulphacetic and disulphometholic acids may be obtained by the action of fuming sulphuric acid on *acetamide* or *acetonitrile*:

$$\underset{\text{Acetonitrile.}}{C^2H^3N} + H^2O + 2H^2SO^4 = \underset{\text{Acid ammonium sulphate.}}{(NH^4)HSO^4} + \underset{\text{Sulphacetic acid.}}{C^2H^4SO^5}$$

$$\underset{\text{Acetonitrile.}}{C^2H^3N} + 3H^2SO^4 = (NH^4)HSO^4 + CO^2 + \underset{\text{Disulphometholic acid.}}{CH^4S^2O^6}$$

In like manner are obtained: from *propionitrile*, C^3H^5N:

Sulphopropionic acid, $C^3H^4(SO^3H).CO^2H$ or $\begin{array}{c}\mathrm{C}\\ |\\ \mathrm{C}\end{array}\left\{\begin{array}{l}H\\ CH^3\\ \underline{SO^3.H}\\ O''\\ OH\end{array}\right.$

Disulphetholic acid, $C^2H^4(SO^3H)^2$ or $C\left\{\begin{array}{l}H\\ CH^3\\ (SO^3H)^2\end{array}\right.$

And from *benzonitrile*, C^7H^5N:

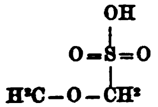
Sulphobenzoic acid, $C^6H^4(SO^3H).CO^2H$
Disulphobenzolic acid, $C^6H^4(SO^3H)^2$.

Sulphobenzolic acid, $C^6H^5(SO^3H)$, is produced by the action of strong sulphuric acid on benzene.

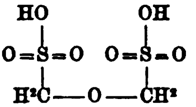
Sulphonaphthalic acid, $C^{10}H^7(SO^3H)$, and *Disulphonaphthalic* acid, $C^{10}H^6(SO^3H)^2$, are obtained by melting naphthalene with strong sulphuric acid or sulphuric anhydride (v. 567).

A sulpho-acid called *methin-trisulphonic acid* (or *methenyl-trisulphonic acid*) containing three equivalents of the radicle SO^3H, and represented by the formula $(CH)'''(SO^3H)^3$, is produced, as a calcium-salt, by heating calcium methylsulphate with fuming sulphuric acid (Theilkuhl, *Ann. Ch. Pharm.* cxvii. 134).

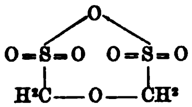
Isethionic acid, $C^2H^6SO^4$, ethionic acid, $C^2H^6S^2O^7$, and ethionic oxide or anhydride, $C^2H^4S^2O^6$, produced by the action of sulphuric anhydride or fuming sulphuric acid on alcohol and ether, likewise belong to this class of bodies, and may be represented by the following formulæ, which show that isethionic acid is monobasic, ethionic acid bibasic, and ethionic oxide neutral:



Isethionic acid.



Ethionic acid.



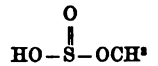
Ethionic oxide.

or:

$$\begin{array}{c}\mathrm{C}\\ |\\ \mathrm{O}\\ |\\ \mathrm{C}\end{array}\left\{\begin{array}{l}\\ \underline{H^3}\\ \overline{H^2}\\ SO^3H\end{array}\right. \qquad \begin{array}{c}\mathrm{C}\\ |\\ \mathrm{O}\\ |\\ \mathrm{C}\end{array}\left\{\begin{array}{l}H^2\\ \underline{SO^3H}\\ \overline{SO^3H}\\ H^2\end{array}\right. \qquad \begin{array}{c}\mathrm{C}\\ |\\ \mathrm{O}\\ |\\ \mathrm{C}\end{array}\left\{\begin{array}{l}H^2\\ SOO\\ SOO\\ H^2\end{array}\right.\!\!\begin{array}{l}\\ O\\ \end{array}$$

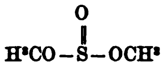
The basicity of a sulpho-acid is equal to the number of atoms of SO^3H and CO^2H together contained in its molecule.

The sulpho-acids formed from hydrocarbons or alcohols are described in the Dictionary as sulphurous ethers (v. 555); but they are perhaps more appropriately represented by the formulæ just given, in all of which the sulphur is represented as in immediate connection with the carbon. In the true sulphurous ethers the sulphur is connected with the carbon only through the medium of oxygen, as in methyl sulphurous acid, $(CH^3)HSO^3$, and neutral methyl sulphite, $(CH^3)^2SO^3$:



$$\overset{\overset{O}{\|}}{HO-S-OCH^3}$$

Methyl sulphurous acid.



$$\overset{\overset{O}{\|}}{H^3CO-S-OCH^3}$$

Neutral methyl sulphite.

Nevertheless, these sulpho-acids resemble the sulphurous ethers in so far that, when treated with alkalis, they are converted into metallic sulphites; and conversely they may be produced by the action of the corresponding chlorides, iodides, &c., on metallic sulphites. For just as ethyl iodide acting on neutral potassium sulphite produces potassium iodide and sulphethylate, according to the equation:

$$C^2H^5I + KSO^3K = C^2H^5.SO^3K + KI;$$

and ethylene bromide with sodium sulphite produces sodium ethylene-sulphite:

$$C^2H^4Br^2 + 2NaSO^3Na = C^2H^4\begin{cases}SO^3Na\\SO^3Na\end{cases} + 2NaBr;$$

so likewise monochloracetic acid with potassium sulphate forms sulphacetate:

$$C^2H^2Cl.CO^2H + KSO^3K = CH^2\begin{cases}SO^3K\\CO^2K\end{cases} + HCl;$$

glycollic monochlorhydrin gives rise to potassium isethionate, $C^2H^4(OH).SO^3K$; glyceric dichlorhydrin produces the potassium salt of disulphoglyceric acid, $C^3H^5(OH).(SO^3H)^2$; and trichlorhydrin produces trisulpho-glyceric acid, $C^3H^5(SO^3H)^3$.

Sometimes, however, the reaction is less simple; thus chloroform at 180° is but slowly attacked by potassium sulphite, carbon dioxide being evolved, together with a gas (methyl chloride?) which burns with a green flame; and the solution contains sulphomethylic acid and its chlorinated derivatives, together with disulphomethylenic and perhaps also trisulphomethylenic acid. In general, however, in the formation of these sulpho-acids by the reaction under consideration, the bromine, chlorine, or iodine united with the carbon is replaced by the univalent radicle SO^3H.

ACOLYCTINE. A base contained, according to Fr. Hübschmann (*Jahresb.* 1866, p. 483), in the root of wolf's bane, *Aconitum lycoctonum*, which does not appear to contain aconitine. It is obtained, together with another base called lycoctonine, by treating the alcoholic extract of the root, first with lime, then with sulphuric acid, evaporating, removing the resin, decolorising with animal charcoal, evaporating to dryness with sodium carbonate, and exhausting the triturated mass with chloroform or absolute alcohol. On digesting the syrupy residue left on evaporating this extract with ether, the lycoctonine dissolves, while the acolyctine, which is present in larger quantity, remains behind. Acolyctine is a whitish powder easily soluble in water, alcohol and chloroform, but insoluble in ether. It has a bitter taste and alkaline reaction, and neutralises acids.

ACONELLINE. This name is given by T. and H. Smith (*Pharm. J. Trans.* [2] v. 317) to a base different from aconitine, which they have extracted from the root of *Aconitum Napellus*.—The mode of preparation is the same as that given below for aconitine, excepting that the sulphuric acid solution is treated, not with ammonia, but with sodium carbonate, added in such quantity as to leave the acid in slight excess. Aconitine then remains dissolved, and the aconelline crystallises after a day or two on the sides of the vessel.

Aconelline differs from aconitine in not being poisonous. It is isomeric with narcotine, exhibiting the same degree of solubility in water, alcohol, &c., the same reactions, and forming a platinum salt in which the percentage of platinum is the same as in platino-chloride of narcotine.

ACONIC ACID. $C^5H^4O^4 = C\begin{cases}(CHCO^2H)''\\(CHCO^2H)''\end{cases}$ (Kekulé, *Ann. Ch. Pharm. Suppl.* i. 338).—An acid produced by the action of alkalis on itadibromopyrotartaric acid (p. 49). When a solution of this acid neutralised with soda is heated to the boiling point, and then gradually mixed with more soda in the proportion of 3 molecules NaHO to 1 molecule of the acid, and the liquid is evaporated, *sodium aconate*, $C^5H^3NaO^4.3H^2O$, crystallises out. This salt is easily soluble in water, and crystallises in thin transparent rhombic tables, which effloresce slowly on exposure to the air. The *barium salt*, $Ba''(C^5H^3O^4)^2$ (at 150°), is formed in a similar manner, and is precipitated in flocks from the concentrated solution by alcohol. The acid is crystallisable and easily soluble in water.

ACONITIC ACID. $C^6H^6O^6 = C^6H^3O^3(OH)^3$.—This acid is formed in very small quantity, together with a volatile acid, when an aqueous solution of citric acid is boiled for 100 hours (Dessaignes, *Bull. Soc. Chim.* [2] v. 355). According to Otto (*Jahresb.* 1863, p. 384), it forms a basic lead-salt containing $Pb^3(C^6H^3O^6)^2.2PbO.2H^2O$ (at 100°).

By the action of sodium amalgam, aconitic acid is converted into tricarballylic acid, $C^6H^8O^6$ (v. 879).

ACONITINE. $C^{30}H^{47}NO^7$.—The best mode of preparing this base in the puro state appears to be that of Hottot (*J. Pharm.* [3] xlv. 304; *Jahresb.* 1863, p. 451). The pulverised root of monkshood is macerated for a week in alcohol of 85 per. cent.; the filtered tincture distilled over the water bath; the aqueous solution of the residue mixed with milk of lime and shaken from time to time; and the filtered solution precipitated with a slight excess of sulphuric acid. The clear liquid filtered from the calcium sulphate is then evaporated to a syrup; the residue is mixed with three or four times its weight of water; and the resulting solution is left at rest, in order to remove a green oil which rises to the surface and solidifies at 20°; the last traces of this oil are removed by pouring it through a wet filter. The filtered liquid is next mixed with ammonia, boiled to expel the excess of that alkali, and render the precipitate more compact; and the precipitate, which is a mixture of aconitine with a resinous matter sparingly soluble in ether, is collected on a filter, washed, dried, and treated with pure ether.

The ethereal solution filtered, and left to evaporate, leaves aconitine still impure. To obtain the alkaloid quite pure, it must be redissolved in dilute sulphuric acid, precipitated by ammonia, and boiled; and the precipitate must be washed, dried, and again treated with ether. By repeating this treatment two or three times, taking care in the last repetition to add the ammonia only drop by drop, so that the first portions of the precipitate, which are still coloured, may be separated, the aconitine is ultimately obtained, white, amorphous, and quite pure: 10 kilogr. of the root thus treated yield from 4 to 6 grms. of pure aconitine (Hottot). According to Procter (*Chem. News*, ix. 87), the root of American monkshood contains 4·2 parts per thousand of aconitine; the European root, only 2 parts per thousand.

Aconitine when cautiously heated yields an amorphous sublimate which in contact with ammonia produces characteristic microscopic crystalline formations, like those of a tin-tree (cruciate needles) (Helwig, *J. Pharm.* [3] xlvi. 459). According to Buignet (*ibid.* xl. 25), it turns the plane of polarisation to the left.

ACORIN. A glucosate extracted from the common reed (*Acorus calamus*). It is soluble in alcohol and ether; precipitated from its ethereal solution by benzene. The alcoholic solution is slightly alkaline. It dissolves in hydrochloric acid, but does not neutralise it (A. Faust, *Bull. Soc. Chim.* [2] x. 392).

ACROLEIN. $C^3H^4O = C^2H^3.COH$.—This compound, the aldehyde of the acrylic series, is formed, together with other products, by the decomposition of acetone dibromide (? dibromisopropyl alcohol) at ordinary temperatures or when heated:

$$C^3H^6OBr^2 = 2HBr + C^3H^4O.$$

Acrolein is converted by *nascent hydrogen* (evolved by zinc and hydrochloric acid) into allyl acohol, isopropyl alcohol, and acropinacone (p. 56) (Linnemann, *Ann. Ch. Pharm. Suppl.* iii. 257):

$$C^3H^4O + H^2 = \underset{\text{Allyl alcohol.}}{C^3H^6O}$$

$$C^3H^4O + 2H^2 = \underset{\text{Isopropyl alcohol.}}{C^3H^8O}$$

$$2C^3H^4O + H^2 = \underset{\text{Acropinacone.}}{C^6H^{10}O^2}$$

A solution of potash (aqueous or alcoholic) saturated with acrolein deposits on addition of an excess of sulphuric acid, brown flocks of hexacrolic acid, and the liquid filtered therefrom yields by distillation a dilute solution of acrylic acid (Claus).

By oxidation with *silver-oxide*, acrolein is converted into acrylic acid, $C^3H^4O^2$; with *potassium bichromate* and *sulphuric acid*, into carbonic and formic acids. With *nitric acid* of sp. gr. 1·2, or with fuming nitric acid, it yields glycollic, together with oxalic acid. By the direct action of *oxygen*, it is only partly converted into disacryl (ii. 336), together with a small quantity of acrylic acid. Heated with *aqueous* or *alcoholic potash* it forms hexacroleic acid, $C^{18}H^{24}O^{6}$ (iii. 151), together with a small quantity of acrylic acid (Claus, *Jahresb.* 1862, p. 245; *Bull. Soc. Chim.* [2] x. 45). This last compound appears also to be formed by treating a mixture of acrolein and ether with sodium ethylate (Alsberg, *ibid.* 1864, p. 487).

Bromine dropped into well-cooled acrolein forms a thick yellow liquid which cannot be distilled alone, but after treatment with alcohol yields by distillation a product passing over between 150° and 170°, and corresponding approximately with the formula $C^{3}H^{4}Br^{2}O$. With *chlorine* in like manner an oil is obtained which yields by distillation a liquid passing over between 150° and 155°, and having nearly the composition $C^{3}H^{4}Cl^{2}O$. *Cyanogen* does not unite with acrolein, but accelerates its resinification (Aronstein, *Ann. Ch. Pharm. Suppl.* iii. 180; *Jahresb.* 1864, p. 332).

With *phosphorus pentachloride*, acrolein yields, besides allylene chloride, $C^{3}H^{4}Cl^{2}$, boiling at 84·5° (i. 56), about an equal quantity of an isomeric compound boiling at 102°, and identical with dihydrochloroglycide or epidichlorhydrin (ii. 896). The portion of the product boiling between 152° and 156° also contains trichlorhydrin, $C^{3}H^{5}Cl^{3}$ (Geuther, *Zeitschr. f. Chem.* 1865, p. 24; *Jahresb.* 1864, p. 333).

Acrolein heated with 2 mol. *acetic chloride* unites with it, forming the compound $C^{7}H^{10}Cl^{2}O^{3} = C^{3}H^{4}O.2C^{2}H^{3}OCl$, a colourless liquid which boils between 140° and 145°, with partial resolution into its component molecules, and decomposes in like manner in contact with water or with alkalis (Aronstein).

Acrolein heated with *ethyl alcohol* and its homologues, and a little acetic acid, yields glyceric ethers: thus, triethylin, $C^{3}H^{5}(C^{2}H^{5})^{3}O^{3}$, is produced by heating 1 vol. acrolein with 1 vol. alcohol and 0·5 vol. acid acid; trimethylin, $C^{3}H^{5}(CH^{3})^{3}O^{3}$, by heating 1 vol. acrolein with 3 vol. methyl alcohol and 0·5 vol. acetic acid; and triamylin, $C^{3}H^{5}(C^{5}H^{11})^{3}O^{3}$, in a similar manner. When *hydrochloric acid gas* is passed into a mixture of acrolein with 2 vols. absolute alcohol, diethyl-chlorhydrin, $C^{3}H^{5}(C^{2}H^{5})^{2}ClO^{2}$, is obtained as a heavy oil of sweetish ethereal odour, and sp. gr. 1·03 at 10·5° (Alsberg, *Jahresb.* 1864, p. 494).

Acrolein acts violently on *aniline*, forming a yellow inodorous amorphous base called diallylidine-diphenamine, $C^{20}H^{18}N^{2} = (C^{6}H^{5})^{2}(C^{3}H^{4})^{2}N^{2}$ (Schiff, *Jahresb.* 1864, p. 414).

Metacrolein has a sp. gr. of 1·03 at 8°, and is therefore not lighter than water, as was formerly supposed (i. 57). With phosphorus pentachloride it yields the same products as acrolein. Heated with acetic anhydride to 150°, it is converted into oily acrolein diacetate, boiling at 180°. It does not unite with ammonia.

ACROLEIN-ACETAL. Syn. with DIETHYL-GLYCIDIC ETHER.

ACROLEIN-AMMONIA. $C^{12}H^{20}N^{2}O^{3}$ (or $C^{12}H^{22}N^{2}O^{4}$ if regarded as analogous to ammonium hydrate).—Claus prepares this compound by directing the vapours of acrolein (produced by the action of acid potassium suphate on glycerin) into aqueous ammonia, then expelling the excess of ammonia by ebullition, and precipitating with alcohol or ether. It acts as a base, forming salts with acids. The hydrochloride has, according to Claus, the composition $C^{12}H^{20}N^{2}O^{2}Cl^{2}$, derived from the hydrate by substitution of Cl^{2} for $(HO)^{2}$.

Acrolein-ammonia is decomposed by dry distillation, yielding, among other products, a liquid base, which forms crystallisable salts. The platino-chloride of this base contains $C^{12}H^{16}N^{2}Cl^{2}.PtCl^{4}$: consequently the free base in the state of hydrate would be $C^{12}H^{18}N^{2}O^{2}$, and would be derived from acrolein-ammonia (also regarded as a hydrate) by elimination of 2 mol. water: $C^{12}H^{22}N^{2}O^{4} - 2H^{2}O = C^{12}H^{18}N^{2}O^{2}$ (Claus, *Ann. Ch. Pharm.* cxxx. 185; *Jahresb.* 1864, p. 416).

According to Schiff (*Ann. Ch. Pharm.* [2] viii. 443), acrolein-ammonia decomposes with excess of acrolein, according to the equation:

$$2N\left\{\begin{matrix}C^{3}H^{4}OH\\ H\\ H\end{matrix}\right. + 2C^{3}H^{4}O = 2H^{2}O + 2N\left\{\begin{matrix}C^{3}H^{4}OH\\ (C^{3}H^{4})''\end{matrix}\right.$$

Acrolein-ammonia. Acrolein.

This base resembles those produced from acetic aldehyde (*q.v.*).

ACROLEIN-OXETHYLCHLORIDE. Syn. with HYDROCHLORIDE OF ETHYL-GLYCIDIC ETHER.

ACROPINACONE. $C^{6}H^{10}O^{2}$ (Linnemann, *Ann. Ch. Pharm. Suppl.* iii. 257).—Produced, together with allylic and isopropylic alcohols, by the action of nascent hydrogen, evolved by zinc and hydrochloric acid, on acrolein. Being insoluble in water, it collects on the surface of the zinc, and thereby impedes the action of the acid: hence it is best to mix the acrolein with half its volume of ether and four times its weight of hydrochloric acid of sp. gr. 1·16, cool it, and pour it immediately on the zinc, which has likewise been cooled. When the action is finished, the acropinacone is dissolved out by repeated agitation with ether, and separated by repeatedly distilling the ethereal solution, and collecting the portion which passes over between 160° and 180°. When recently distilled it is colourless, but gradually turns brown on exposure to the air. It has a peculiar camphorous odour, a sp. gr. of 0·99 at 17°, is insoluble in water, but dissolves easily in alcohol and ether. It is related to acrolein in the same manner as pinacone to acetone, or benzopinacone to benzophenone (iv. 617).

ACROTHIALDINE. $C^9H^{13}NS^2 = N\begin{cases}C^3H^4SH\\C^3H^4SH.\\C^3H^3\end{cases}$—A base produced by the action of ammonium sulphydrate on acrolein (Schiff, *Bull. Soc. Chim.* [2] viii. 444). (See THIALDINE.)

ACRYLIC ACID. $C^3H^4O^2 = CH(CH^2)''.CO^2H$.—This acid, produced by the direct oxidation of acrolein and of allyl alcohol, is also formed, according to Butlerow (*Ann. Ch. Pharm.* cxiv. 204), together with other products, by the action of iodoform on sodium ethylate. An alcoholic solution of baryta, kept for several years in badly closed bottles, was found by Berthelot (*Jahresb.* 1863, p. 395) to contain an acid isomeric or identical with acrylic acid, together with aldehyde-resin and oxalic acid.

According to Claus (*Ann. Ch. Pharm. Suppl.* ii. 117), the best mode of preparing this acid is to treat acrolein, mixed with 3 vols. water, with recently precipitated silver oxide, as in Redtenbacher's process (i. 57); heat the liquid to the boiling point, after the odour of acrolein has disappeared; add sodium carbonate to slight alkaline reaction; evaporate to dryness; and decompose the residue with sulphuric acid. On distilling the filtrate, acrylic acid passes over as a colourless strongly acid liquid.

Acrylic acid treated with powerful oxidising agents, such as chromic acid, is converted into acetic and formic acids; heated with caustic potash, it yields formate and acetate, with evolution of hydrogen (p. 41).

Acrylic acid in aqueous solution takes up 1 mol. bromine, and forms dibromopropionic acid, $C^3H^4Br^2O^2$, which may be crystallised by slow evaporation (Wichelhaus, *Jahresb.* 1867, p. 403).

The acrylates, excepting the silver salt, are easily soluble in water. They are best prepared by neutralising the acid with sodium carbonate; the solution, even when prepared with perfectly colourless acid, turns yellow, and must be decolorised by animal charcoal. The acrylates, when heated to 100°, all give off part of their acid, and leave basic salts; the potassium, barium, and zinc salts undergo this decomposition, even at ordinary temperatures. The *potassium salt*, $KC^3H^3O^2$, and the *sodium salt*, $NaC^3H^3O^2$, form indistinctly crystalline masses. The *silver salt*, $AgC^3H^3O^2$, forms a curdy precipitate, or lancet-shaped needles; it is moderately soluble in boiling water, and easily reducible. The *barium salt* is gummy, and forms needle-shaped crystals, only after its colourless solution has been left to stand for a long time. The *calcium salt*, $Ca''(C^3H^3O^2)^2$, remains on evaporation in groups of small, thick needles, which gradually become opaque, and easily lose their acid. The *lead salt*, $Pb''(C^3H^3O^2)^2$, crystallises from a hot aqueous solution, or better by evaporation under the air-pump, in stellate groups of shining needles, often half an inch long. The *zinc salt*, $Zn''(C^3H^3O^2)^2$, remains on evaporation in small scales, which do not redissolve completely in water. *Ethylic acrylate* is not produced by heating the lead-salt with ethylic iodide, the salt being in fact resolved into acrylic acid and a basic salt before the ethylic iodide can act upon it (Claus).

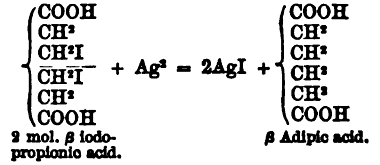
ACRYLIC SERIES OF ACIDS. See p. 40.

ADAMINE. A hydrated zinc arsenate, occurring in a compact limestone at Chanarcillo, in Chile, in honey-yellow grains having a bright vitreous lustre, or in very small violet-coloured right rhombic prisms, having an octohedral character, and exhibiting the combination $\infty P . \infty\bar{P}2 . \infty\breve{P}2 . \infty\breve{P}\infty . \bar{P}\infty . P$, the macrodome predominating, and P being observed only on a few cleavage-faces; most of the faces exhibit wavy striations. Cleavage distinct, parallel to $\bar{P}\infty$. Angle $\infty P : \infty P = 91° 52'$; $\infty\bar{P}2 : \infty\bar{P}2 = 128° 6'$; $\bar{P}\infty : \bar{P}\infty$ over the principal axis = 107° 20′. The crystals are optically positive, the plane of the optic axes being parallel to oP, and the median line perpendicular to $\infty\breve{P}\infty$. The crystals scratch calcspar, but are scratched by fluorspar. Sp. gr. = 4·338. Analysis gave 39·85 p. c. As^2O^5, 54·32 ZnO, 1·48 FeO, with trace of MnO, and 4·55 water (= 100·20), whence the formula $4ZnO.As^2O^5.H^2O$, or $AsZn^2H^2O^5$ or $(AsO)'''Zn^2H^2O^4$ (C. Friedel, *Bull. Soc. Chim.* [2] v. 433).

ADIPIC ACID. $C^6H^{10}O^4$.—This acid, the fifth of the oxalic series, $C^nH^{2n-2}O^4$ (p. 47), is produced, according to Crum-Brown (*Bull. Soc. Chim.* 1863, p. 372), by heating mucic acid with hydriodic acid and phosphorus to 140° in a sealed tube for twenty hours:

$$C^6H^{10}O^8 + 8HI = C^6H^{10}O^4 + 4I^2 + 4H^2O.$$

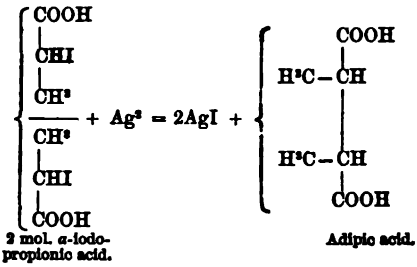
L. Marquardt (*Zeitschr. f. Chem.* [2] v. 635) obtains it by the action of sodium amalgam on muconic acid, $C^6H^6O^4$ (v. 1093). Wislicenus (*ibid.* iv. 680), by heating Beilstein's β iodopropionic acid to 150°, with excess of finely divided silver or copper, obtains an isomeride of adipic acid, and represents its formation by the following equation:



$$\left\{\begin{array}{l}COOH\\ CH^2\\ CH^2I\\ \hline CH^2I\\ CH^2\\ COOH\end{array}\right. + Ag^2 = 2AgI + \left\{\begin{array}{l}COOH\\ CH^2\\ CH^2\\ CH^2\\ CH^2\\ COOH\end{array}\right.$$

2 mol. β iodo-propionic acid. β Adipic acid.

α-Iodopropionic acid treated in like manner yields ordinary or α-adipic acid:



$$\left\{\begin{array}{l}COOH\\ |\\ CHI\\ |\\ CH^3\\ \hline CH^3\\ |\\ CHI\\ |\\ COOH\end{array}\right. + Ag^2 = 2AgI + \left\{\begin{array}{l}\quad\;\; COOH\\ \quad\quad |\\ H^3C-CH\\ \quad\quad |\\ H^3C-CH\\ \quad\quad |\\ \quad\;\; COOH\end{array}\right.$$

2 mol. α-iodo-propionic acid. Adipic acid.

(Wislicenus, *ibid.* vi. 247).

According to Arppe (*Acta Scientiarum Societatis fennicæ*, viii.; *Jahresb.* 1864, p. 377), adipic acid is produced by the oxidation of sebic or sebacic acid with nitric acid, and is identical with the acid formerly called *oxypyrolic acid* (iv. 319). It is also found in small quantity in the more soluble pertion of the products of oxidation of the fatty acids, $C^nH^{2n}O^4$. It crystallises in vitreous brittle laminæ or prismatic flattened needles, melts at 148°, sublimes undecomposed as a crystalline powder when cautiously heated, and dissolves easily in warm water, alcohol, and ether. Its salts were found to exhibit the following characters:

Potassium adipate	$C^6H^8K^2O^4.C^6H^9KO^4$	confused crystalline mass.
Sodium „	$C^6H^8Na^2O^4.2H^2O$	easily soluble crystalline mass.
Silver „	$C^6H^8Ag^2O^4$	crystalline powder.
Barium „	$C^6H^8BaO^4$	granular powder.
Calcium „	$C^6H^8CaO^4.H^2O$	precipitate on boiling.
Cadmium „	$C^6H^8CdO^4.2H^2O$	moderately distinct crystals.
Copper „	$C^6H^8CuO^4$	green precipitate.
Lead „	$C^6H^8PbO^4$	brown-red flocculent precipitate.

Ammonium adipate forms large monoclinic augitic crystals, which between 130° and 150° are converted (with further decomposition) into a crystalline powder (adipamide) soluble in water. ***Ethylic adipate*** distils unaltered at 245°, and is not decomposed by ammonia (Arppe).

ÆSCHYNITE. According to recent analyses by Marignac (*Bull. Soc. Chim.* [2] viii. 179), this mineral consists essentially of titano-niobate of thorinum and cerium, with smaller quantities of lanthanum, didymium, yttirum, and iron.

Nb^2O^5 and TiO^2	SnO^2	ThO	CeO	LaO a. DiO	YO	FeO	CaO	Loss
51·45	0·18	15·75	18·49	5·60	1·12	3·17	2·75	1·07 = 99·58

The ratio of the acid oxides appears to be 56·96 niobic to 43·04 titanic oxide, or $2Nb^2O^5 : 5TiO^2$, the same as in euxenite. Hence Marignac concludes that these two minerals may be included in the general formula:

$$5(MO.TiO^2) + 2(2MO.Nb^2O^5).$$

He was unable to find any evidence of the existence of Hermann's ilmenium in this mineral. (For Hermann's analyses, see *Jahresb.* 1865, p. 897; 1866, p. 945.)

ÆSCINIC ACID, ÆSCIGENIN, ÆSCIGLYCOLLIC ACID, ÆSCIORCIN, ÆSCULETIN, &c. See ÆSCULUS.

ÆSCULIC ACID. Rochleder (*Bull. Soc. Chim.* [2] ix. 387) assigns to this acid the formula $C^{26}H^{42}O^{12}$, and explains its formation from saponin by the equation:

$$C^{32}H^{54}O^{18} = C^{26}H^{42}O^{12} + C^{6}H^{12}O^{6}.$$

ÆSCULUS. Rochleder (*Wien. Akad. Ber.* lv.; *Bull. Soc. Chim.* [2] ix. 383) has made further experiments on the chemical composition of the seeds of the horse-chestnut (*Æsculus hippocastanum*). He regards the proximate principles of these seeds, with their derivatives, as forming a series parallel to glycol and its derivatives; thus:

Glycol	$C^{2}H^{6}O^{2}$	Æsciglycol	$C^{7}H^{10}O^{2}$
Glycolal	$C^{2}H^{4}O^{2}$	Æsciglycolal	$C^{7}H^{8}O^{2}$
Glycollic acid	$C^{2}H^{4}O^{3}$	Æsciglycollic acid	$C^{7}H^{8}O^{3}$
Glyoxal	$C^{2}H^{2}O^{2}$	Æsciglyoxal	$C^{7}H^{6}O^{2}$
Glyoxalic acid	$C^{2}H^{2}O^{3}$	Æsciglyoxalic acid	$C^{7}H^{6}O^{3}$
Oxalic acid	$C^{2}H^{2}O^{4}$	Æscioxalic acid	$C^{7}H^{6}O^{4}$

Horse-chestnut seeds contain æscigenin, $C^{12}H^{20}O^{2}$,* homologous with æsciglycol; æsciglyoxal is present in the form of æsculetin, $C^{9}H^{6}O^{4}$, derived from it by substitution of two atoms of formyl, CH for H^{2}; æsciglyoxalic acid combined with phloroglucin constitutes the tannin of the horse-chestnut.

Æsciglycollic acid was obtained by Hlasiwetz by the action of sodium-amalgam on quercetin. Æscioxalic acid is formed by the action of potash on æsculetin, together with æscorcin, $C^{9}H^{8}O^{4}$, which has the composition of diformylic æsciglycolal. Æscigenin is contained in the cotyledons in three different states, viz. as æscinic acid, argyrescin and aphrodescin (iii. 172).

Strong boiling potash-ley or baryta-water decomposes æsculetin into formic, oxalic and æscioxalic acids, the last being isomeric with protocatechuic acid; and if the reaction be performed in an atmosphere of hydrogen replaced at the last by carbonic acid gas to precipitate the excess of baryta, a solution of a barium salt is obtained, which when decomposed by sulphuric acid yields æscioxalic acid in colourless microscopic crystals containing $C^{7}H^{6}O^{4}.H^{2}O$.

Æsculetin unites with acid sodium sulphite, forming the compound $C^{9}H^{6}O^{4}.NaHSO^{3}.\frac{1}{2}H^{2}O$, from which the æsculetin cannot be recovered in its original state: in fact, the sodium compound when decomposed by an alkali yields an isomeric body; paræsculetin, which has the nature of an aldehyde, dissolves sparingly in water, more freely in alcohol, very easily in water, and crystallises confusedly when the solution is evaporated in a vacuum. The crystals contain $2C^{9}H^{6}O^{4}.5H^{2}O$ and require a high temperature to deprive them of their water. Paræsculetin exposed to an atmosphere of ammonia immediately becomes red, then violet, and ultimately yields a sky-blue liquid, which in presence of sulphuric acid gives off the excess of ammonia and becomes red again. This ammoniacal compound forms a copper-coloured lead-salt containing $3(2C^{9}H^{7}NO^{5}.H^{2}O).10PbO$, which gives off water at 100°. The blue substance is therefore composed of $C^{9}H^{7}NO^{5}$, and appears to be formed according to the equation:

$$C^{9}H^{6}O^{4} + NH^{3} + O^{2} = C^{9}H^{7}NO^{5} + H^{2}O.$$

From its analogy to orcein, Rochleder calls it æsorcein.

Æsculetin unites with nascent hydrogen; when treated with sodium amalgam it forms a liquid which turns red on exposure to the air; but the presence of sulphuric acid prevents the coloration. If the fixation of hydrogen be effected in a solution acidulated with sulphuric acid, an amorphous substance is obtained which may be extracted by ether, and whose aqueous solution forms with lead nitrate a yellow precipitate, turning red in the air, as likewise does the solution, which yields a white precipitate with basic lead acetate. This last precipitate contains an acid isomeric with Hlasiwetz's caffeic acid, $C^{9}H^{8}O^{4}$, and having the composition of orcin, ($C^{7}H^{8}O^{2}$), with $C^{2}O^{2}$ added to it: hence called æsorcin. It dissolves in alkalis with green colour, quickly changing to red. When exposed in the moist state to the action of ammonia gas it is rapidly converted into æsorcein.

Æsculetin reduces the dioxides of lead and manganese, mercuric oxide, and alkaline cupric solutions; it is strongly attacked by chromic and nitric acids, forming amorphous bodies, which are difficult to separate. With silver oxide as the oxidising agent, a brown resinous substance is formed, together with a difficultly crystallisable body isomeric with æsculetin.

Horse-chestnut seeds sometimes contain, instead of argyræscin,† $C^{27}H^{42}O^{12}$, another substance containing C^2H^2 less. This substance, if treated first with potash, then with hydrochloric acid in alcoholic solution, yields, not æscigenin, but a diatomic alcohol, $C^{11}H^{18}O^2$ (Rochleder, *Wien. Akad. Ber.* lvi.; *Bull. Soc. Chim.* [2] ix. 385).

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* Rochleder formerly assigned to this body the formula $C^{24}H^{20}O^{4}$ (iii. 172).

† Rochleder formerly assigned to this substance the formula $C^{54}H^{42}O^{24}$ (see iii. 172).

AGAVE. Well-preserved juice of *Agave americana*, of sp. gr. 1·046 at 15·2°, was found by J. Boussingault (*Ann. Ch. Phys.* [4] xi. 447) to contain in 1,000 parts:

Levulose	26·45	Albumin	10·13
Cane sugar	61·71	Ammonia	0·06
Malic acid	3·53	Inorganic substances	6·21
Gum	5·45	Water	886·46

The fermented liquid (*pulque*), obtained by the action of yeast on the juice, concentrated and then again diluted nearly to its original strength, was found to contain in a litre, 35·4 grms. alcohol, a quantity of organic acids equivalent to 1·60 grm. sulphuric acid (H^2SO^4) and 0·04 grm. ammonia, but it no longer contained sugar. It was turbid and had a faint vinous odour, but not the disagreeable smell peculiar to *Pulque fuerte*, which this liquid acquires only after standing for a long time over the abundantly separated yeast.

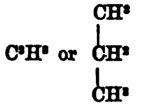
AKAZGA. A poison used in Western Africa, and obtained apparently from a loganaceous plant. It was exported in long delicate tortuous twigs, containing, between the bark and the wood, a few crystals which have not been examined. The alcoholic extract of the bark, treated according to the method of Stas for the discovery of alkaloïds, yielded an active principle amounting to 2 per cent. of the weight of the bark. This substance is an alkaloïd, soluble in 60 pts. of cold absolute alcohol, in 16 pts. of spirit of 85 per cent., in 120 pts. of anhydrous ether, and in 13,000 pts. of cold water; it dissolves also in chloroform, carbon bisulphide and benzene. The alcoholic solution, slowly evaporated, deposits small prisms. The molecular weight of the base, deduced from the analysis of its hydrochloride and platinochloride, is between 290 and 293. This base, when heated, turns yellow, melts, and decomposes, giving off irritating vapours. Its salts are very bitter and yield amorphous precipitates with alkalis, alkaline carbonates, and most of the other reagents which precipitate alkaloïds. Chlorine forms a white precipitate soluble in ammonia. A mixture of sulphuric acid and potassium bichromate produces the same reaction as with strychnine (Fraser, *J. pr. Chem.* civ. 51; *Bull. Soc. Chim.* [2] xi. 176).

ALCEA. The Mexican plant *Alcea rosea* (*passe-rose*) yields a substance intermediate in its properties between the fats and resins. This substance, called by the natives *Obreguin*, is produced by the puncture of an insect on the branches. It is nearly insoluble in alcohol, easily soluble in ether, turpentine-oil, and chloroform, and remains on evaporation of its solutions as a colourless, inodorous, terebinthaceous mass, easily saponified by alkalis (Dauzats, *J. Pharm.* [4] v. 174).

ALCOGEL. The gelatinous compound of alcohol with silicic acid. (See Colloïdal Acids, in Appendix, v. 1089.)

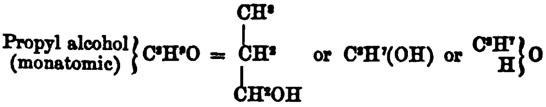
ALCOHOL (ordinary). See Ethyl Alcohol.

ALCOHOLS. An alcohol may be derived from a hydrocarbon containing an even number of hydrogen atoms by the substitution of one or more equivalents of hydroxyl, HO, for an equal number of hydrogen atoms, the alcohol being monatomic, diatomic, triatomic, &c., according to the number of equivalents of hydroxyl thus introduced. Alcohols may of course be likewise regarded as compounds of hydroxyl with hydrocarbon-radicles (alcohol-radicles), univalent or multivalent, or again as derived from one or more molecules of water, by substitution of such a radicle for an equivalent number of hydrogen atoms. Thus from propane or propyl hydride,

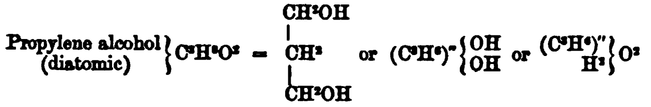


$$C^3H^8 \text{ or } \begin{array}{l} CH^3 \\ | \\ CH^2 \\ | \\ CH^3 \end{array}$$

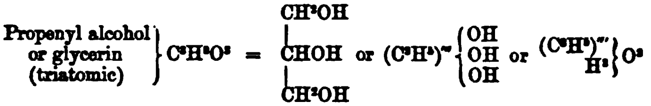
are derived the three following alcohols:



$$\left.\begin{array}{r}\text{Propyl alcohol} \\ \text{(monatomic)}\end{array}\right\} C^3H^8O = \begin{array}{l} CH^3 \\ | \\ CH^2 \\ | \\ CH^2OH \end{array} \text{ or } C^3H^7(OH) \text{ or } \left.\begin{array}{r} C^3H^7 \\ H \end{array}\right\} O$$



$$\text{Propylene alcohol (diatomic)}\ C^3H^8O^2 = \begin{array}{c} CH^2OH \\ | \\ CH^2 \\ | \\ CH^2OH \end{array} \text{ or } (C^3H^6)''\left\{\begin{array}{l} OH \\ OH \end{array}\right. \text{ or } \left.\begin{array}{r} (C^3H^6)'' \\ H^2 \end{array}\right\} O^2$$



$$\text{Propenyl alcohol or glycerin (triatomic)}\ C^3H^8O^3 = \begin{array}{c} CH^2OH \\ | \\ CHOH \\ | \\ CH^2OH \end{array} \text{ or } (C^3H^5)'''\left\{\begin{array}{l} OH \\ OH \\ OH \end{array}\right. \text{ or } \left.\begin{array}{r} (C^3H^5)''' \\ H^3 \end{array}\right\} O^3$$

An alcohol is saturated or unsaturated according to the nature of the hydrocarbon from which it is derived. Thus all the three alcohols derived from propane, C^3H^8, which is a saturated hydrocarbon, are themselves saturated molecules, not capable of forming new compounds by addition; but from the unsaturated hydrocarbon $(C^3H^6)''$ is derived the unsaturated compound allyl alcohol, C^3H^6O or $C^3H^5(OH)$, which is capable of taking up 2 at. bromine and forming the compound $C^3H^6Br^2O$. In like manner, all the allyl-compounds formed on the type C^3H^5R (the symbol R denoting a monatomic acid or chlorous radicle) can take up two additional atoms of such radicle or radicles, whereby they are converted into compounds of the propenyl or glyceryl group $(C^3H^5)'''R^3$. (See ALLYL-COMPOUNDS, i. 141, 142.)

The substitution of an alcohol-radicle for the hydrogen of either of the groups OH in an alcohol converts it into an ether, and the number of ethers which an alcohol can form with the same alcohol-radicle is determined by the number of equivalents of hydroxyl contained in its molecule (see p. 38).

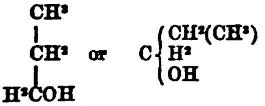
The substitution of O for H^2 in one or more of the groups H^2OH converts the alcohol into an acid, and the removal of 2 atoms of hydrogen from one of these groups without replacement by oxygen converts the alcohol into an aldehyde.

Most of the known alcohols are enumerated and classified in the article ALCOHOLS, vol. i. pp. 97–104. There are however some additions to be made, especially relating to isomeric modifications.

MONATOMIC ALCOHOLS.

a. **Series** $C^nH^{2n+2}O$ or $C^nH^{2n+1}(OH)$.—To the list of these alcohols given in the article just referred to must be added nonyl alcohol, $C^9H^{20}O$, formed from the nonyl hydride, C^9H^{20}, occurring in American petroleum, by converting that compound first into chloride, then into acetate, and distilling the latter with potash (iv. 134). The alcohols containing 12, 14 and 16 atoms of carbon are supposed to exist in spermaceti, together with sexdecyl or cetyl alcohol, because that substance when fused with potash-lime yields the corresponding fatty acids $C^nH^{2n}O^2$ (Heintz, *Pogg. Ann.* lxxxiv. 232; lxxxvii. 553).

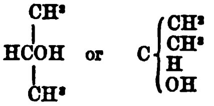
The isomeric modifications of these alcohols, *primary*, *secondary*, and *tertiary*, have already been noticed in the article SECONDARY AND TERTIARY ALCOHOLS, by Professor Wanklyn, in vol. v. pp. 215–218. It is there stated that *an alcohol is said to be primary, secondary, or tertiary, according as the carbon-atom which is in combination with hydroxyl is likewise directly combined with one, two, or three other carbon-atoms.* The first and second alcohols of the series can exist in one form only, but the three-carbon alcohol admits of two modifications, viz.,



$$\begin{array}{c} CH^3 \\ | \\ CH^2 \\ | \\ H^2COH \end{array} \text{ or } C\left\{\begin{array}{l} CH^2(CH^3) \\ H^2 \\ OH \end{array}\right.$$

Normal propyl alcohol.

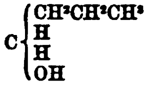
and



$$\begin{array}{c} CH^3 \\ | \\ HCOH \\ | \\ CH^3 \end{array} \text{ or } C\left\{\begin{array}{l} CH^3 \\ CH^3 \\ H \\ OH \end{array}\right.$$

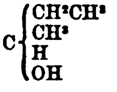
Isopropyl alcohol.

and the four-carbon alcohol of three modifications, viz.,



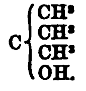
$$C\left\{\begin{array}{l} CH^2CH^2CH^3 \\ H \\ H \\ OH \end{array}\right.$$

Primary.



$$C\left\{\begin{array}{l} CH^2CH^3 \\ CH^3 \\ H \\ OH \end{array}\right.$$

Secondary.



$$C\left\{\begin{array}{l} CH^3 \\ CH^3 \\ CH^3 \\ OH. \end{array}\right.$$

Tertiary.

The five-carbon alcohol and those above it are also susceptible of three similar modifications; but modifications higher than the tertiary are impossible, inasmuch as the carbon-atom associated with hydroxyl by one of its atomicities or units of equivalence has only three others to dispose of.

There is still, however, another kind of modification of which the alcohols of each of these three groups are susceptible, arising from modifications in the alcohol-radicles themselves. (See HYDROCARBONS.) The primary four-carbon alcohol, for example, may be represented by either of the formulæ:

$$C\left\{\begin{array}{l} CH^2CH^2CH^3 \\ H \\ H \\ OH \end{array}\right. \qquad C\left\{\begin{array}{l} CH(CH^3)^2 \\ H \\ H \\ OH \end{array}\right.$$

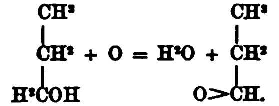
Each of these fulfils the essential condition of a primary alcohol; but the first contains normal propyl, $CH^2(C^2H^5)$, whereas the second contains isopropyl, $CH(CH^3)^2$; and in the higher alcohols it is easy to see that a still larger number of modifications may exist.

A very convenient nomenclature for these isomeric alcohols has been proposed by Kolbe. Methyl alcohol, $CH^3(OH)$, is called **carbinol**; and the primary alcohols formed from it by successive substitution of methyl, ethyl, &c., for an atom of hydrogen are named according to the radicles which they contain; thus:

Carbinol	C	OH	H	H	H
Methyl carbinol or Ethyl alcohol	C	OH	H	H	CH^3
Ethyl carbinol or Propyl alcohol	C	OH	H	H	$(CH^2CH^3)'$
Dimethyl carbinol or Isopropyl alcohol . . .	C	OH	H	CH^3	CH^3
Propyl carbinol or Butyl alcohol	C	OH	H	H	$(CH^2CH^2CH^3)'$
Isopropyl carbinol or Isobutyl alcohol . . .	C	OH	H	H	$[CH(CH^3)^2]'$
Methyl-ethyl carbinol or Secondary Butyl alcohol .	C	OH	H	CH^3	$(CH^2CH^3)'$
Trimethyl carbinol or Tertiary Butyl alcohol . .	C	OH	CH^3	CH^3	CH^3.

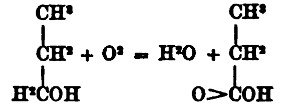
It will be observed that the four-carbon alcohol admits of four modifications, two primary, one secondary, and one tertiary. In like manner it will be found that the five-carbon alcohol admits of eight modifications, and the higher alcohols of a still greater number; but only a few of these modifications are actually known.

All the primary alcohols contain the group CH^2OH, and are converted by oxidation into aldehydes and acids containing the same number of carbon-atoms; thus:



$$\begin{array}{c} CH^3 \\ | \\ CH^2 \\ | \\ H^2COH \end{array} + O = H^2O + \begin{array}{c} CH^3 \\ | \\ CH^2 \\ | \\ O{>}CH. \end{array}$$

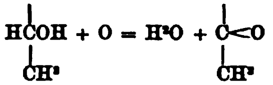
Propyl alcohol. Propionic aldehyde.



$$\begin{array}{c} CH^3 \\ | \\ CH^2 \\ | \\ H^2COH \end{array} + O^2 = H^2O + \begin{array}{c} CH^3 \\ | \\ CH^2 \\ | \\ O{>}COH \end{array}$$

Propyl alcohol. Propionic acid.

The secondary alcohols, on the other hand, contain two equivalents of alcohol-radicle combined with the group CHOH, and are converted by oxidation into ketones; e.g.,



$$\begin{array}{c} CH^3 \\ | \\ HCOH \\ | \\ CH^3 \end{array} + O = H^2O + \begin{array}{c} CH^3 \\ | \\ C{<}O \\ | \\ CH^3 \end{array}$$

Isopropyl alcohol. Acetone.

The tertiary alcohols contain three equivalents of alcohol-radicle associated with COH, and are converted by oxidation into two or more acids containing smaller numbers of carbon-atoms.

Primary Alcohols.—The synthetic methods of forming the alcohols of the three classes are given in the article in vol. v. above referred to.. The methods of building up the **primary alcohols** one from the other through the medium of the fatty acids and aldehydes are mentioned on p. 39 of this volume. The method depending on the action of nitrous acid on the corresponding amines (iii. 164) cannot for the present be regarded as perfectly general, inasmuch as it has not yet been found possible to prepare normal propyl alcohol by it (v. 888) (Linnemann, *Ann. Ch. Pharm.* cxliv. 129).

Linnemann finds, moreover, that the method proposed by Hofmann (conversion of the base by excess of nitrous acid into the corresponding nitrous ether) does not yield good results, because the nitrous ether is produced in small quantity only, and is for the most part carried away by the nitrogen gas, which is evolved in great abundance. Better results are obtained by decomposing the nitrites of the amine-bases by application of heat to their slightly acidulated solutions. The best mode of proceeding is to prepare the nitrite of the amine-base by decomposing the hydrochloride with silver nitrite, filtering from silver chloride, and boiling the slightly acidulated filtrate in a distillatory apparatus. The decomposition takes place below the boiling heat, with formation of nitrogen, water, and an alcohol, and if the liquid is kept slightly acid, it is nearly complete. The formation of an alcohol in this process appears to be almost always accompanied by that of a nitrogenous substance. In one experiment, Linnemann obtained from 15·5 grms. ethylamine, 4 grms. of pure ethyl alcohol boiling between 78° and 79°, about 2 grms. of a neutral yellowish substance boiling at 170°–172°, and having the composition $C^4H^{10}N^2O$, and 1 grm. of a mixture of this substance with alcohol.

Other recently discovered methods of forming the primary alcohols of this series are the following:

α. By the action of nascent hydrogen (sodium amalgam and water applied in succession) on the corresponding acid oxides or anhydrides: e.g.,

$$\underset{\text{Acetic oxide.}}{(C^2H^3O)^2O} + 4H^2 = H^2O + \underset{\text{Ethyl-alcohol.}}{2C^2H^6O}$$

In like manner propionic oxide has been converted into propyl alcohol (Linnemann, *Zeitschr. f. Chem.* [2] v. 143).

β. By the action of sodium amalgam on a mixture of a fatty acid with the corresponding chloride: thus acetic acid and acetic chloride yield ethyl alcohol. Propyl and butyl alcohol have been prepared in a similar manner (Saytzeff, *ibid.* v. 551; vi. 105).

γ. According to Veiel, the fatty acids may be converted by oxidation with manganese dioxide and dilute sulphuric acid into compound ethers, from which the corresponding alcohols may be obtained. (See Acids, Organic, p. 40.)

The alcohols produced by fermentation, and those obtained from the paraffins or alcoholic hydrides, C^nH^{2n+2}, by converting these hydrides into chlorides, the latter into acetates, and distilling the acetates with potash, must be regarded as primary alcohols, because they exhibit the essential character of those alcohols, viz. that of yielding by oxidation fatty acids and aldehydes containing the same number of carbon-atoms.

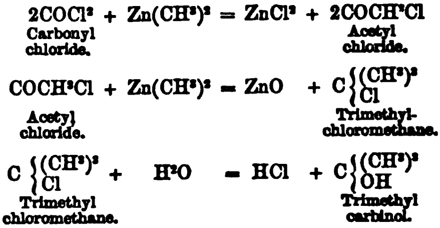
The structure of the radicle in a primary alcohol may be determined in some cases by that of the fatty acid produced from it. The first three primary alcohols of the series $CH^3(OH)$, $CH^3CH^2(OH)$, and $CH^3CH^2CH^2(OH)$, admit of no modifications. Of the four-carbon alcohol, as already observed, there are two modifications, viz. propyl-carbinol and isopropyl-carbinol (p. 62). The first of these is produced, according to Schöyen (*Ann. Ch. Pharm.* cxxx. 283), from diethyl, C^4H^{10} (butyl-hydride), by converting this compound into the chloride and acetate as above described, and distilling the acetate with barium hydrate. The butylic alcohol thus obtained was converted by oxidation with potassium bichromate and sulphuric acid, into normal butyric or ethyl-acetic acid, $CH^3CH^2CH^2.CO^2H$ (p. 40): hence the alcohol itself has the composition of propyl-carbinol, $CH^3CH^2CH^2.CH^2OH$. Lieben a. Rossi (*Compt. rend.* lxviii. 1561) have lately obtained this same alcohol by the action of sodium amalgam on butyric aldehyde.

Isopropyl carbinol, $CH(CH^3)^2.CH^2OH$, is the variety of butyl alcohol found by Wurtz in the fusel-oil obtained by fermenting the molasses of beet-sugar (see v. 738, where it is designated as normal butylic or tetrylic alcohol). When oxidised in the manner above mentioned, it yields isobutyric or dimethyl-acetic acid, $CH(CH^3)^2.COOH$ (p. 40). See, further, Butyl Compounds, in this volume.

The primary 5-carbon or amyl alcohol, $C^5H^{12}O = C^4H^9.CH^2OH$, is susceptible of four modifications, accordingly as the radicle C^4H^9 takes the form $CH^2CH^2CH^2CH^3$, or $CH^2CH(CH^3)^2$, or $CH(CH^3)(C^2H^5)$, or $C(CH^3)^3$. The first of these, or normal amyl alcohol, has quite recently been obtained from normal butyl alcohol by a synthetical process to be described further on. The second, as shown by Erlenmeyer, is the ordinary amyl alcohol of fermentation; and this again, as shown some years ago by Pasteur, exhibits two modifications closely resembling one another in most of their properties, but differing in their relations to polarised light; these however are probably only physical modifications of one and the same chemical compound (see Amyl

Tertiary Alcohols. $C^nH^{2n+2}O$.—The known compounds of this group contain four, five, and six atoms of carbon.

Tertiary butyl alcohol or trimethyl carbinol, $C\left\{\begin{matrix}(CH^3)^3\\ OH\end{matrix}\right.$, is produced by heating zinc-methyl with carbonyl chloride (phosgene) or with acetyl chloride, and submitting the product to the action of water:



$$\underset{\text{Carbonyl chloride.}}{2COCl^2} + Zn(CH^3)^2 = ZnCl^2 + \underset{\text{Acetyl chloride.}}{2COCH^3Cl}$$

$$\underset{\text{Acetyl chloride.}}{COCH^3Cl} + Zn(CH^3)^2 = ZnO + \underset{\text{Trimethyl-chloromethane.}}{C\left\{\begin{matrix}(CH^3)^3\\ Cl\end{matrix}\right.}$$

$$\underset{\text{Trimethyl chloromethane.}}{C\left\{\begin{matrix}(CH^3)^3\\ Cl\end{matrix}\right.} + H^2O = HCl + \underset{\text{Trimethyl carbinol.}}{C\left\{\begin{matrix}(CH^3)^3\\ OH\end{matrix}\right.}$$

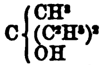
According to Butlerow (*Bull. Soc. Chim.* [2] viii. 268), it is contained in the commercial butylic alcohol, prepared at Wyl, Canton St. Gall, and is therefore also a product of fermentation.

The properties of the alcohol have not been much studied. By oxidation with dilute chromic acid it is converted into formic and propionic acids:

$$C^4H^{10}O + O^4 = CH^2O^2 + C^3H^6O^2 + H^2O.$$

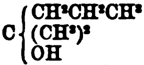
A tertiary amyl alcohol or dimethyl-ethyl carbinol, $C(CH^3)^2(C^2H^5).OH$, is produced in like manner by means of zinc-methyl and propionyl chloride.

Of **tertiary hexyl alcohols** there may be three varieties, viz.,



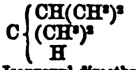
$$C\left\{\begin{matrix}CH^3\\ (C^2H^5)^2\\ OH\end{matrix}\right.$$

Methyl-diethyl carbinol.



$$C\left\{\begin{matrix}CH^2CH^2CH^3\\ (CH^3)^2\\ OH\end{matrix}\right.$$

Propyl-dimethyl carbinol.



$$C\left\{\begin{matrix}CH(CH^3)^2\\ (CH^3)^2\\ H\end{matrix}\right.$$

Isopropyl-dimethyl carbinol.

The third has not yet been obtained. The first is prepared by treating zinc-ethyl with acetyl chloride and decomposing the resulting methyl-diethyl-chlorethane, $C\left\{\begin{matrix}CH^3\\ (C^2H^5)^2\\ Cl\end{matrix}\right.$, with water; the second by proceeding in like manner with zinc-ethyl and butyryl chloride, $CO(C^3H^7)Cl$.

β. **Monatomic Alcohols.** $C^nH^{2n}O$.—Two alcohols of this series are known, viz.,

Vinyl alcohol, $C^2H^4O = C^2H^3(OH)$
Allyl alcohol, $C^3H^6O = C^3H^5(OH)$.

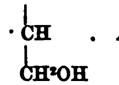
The first, discovered by Berthelot in 1860 (*Compt. rend.* l. 805), is produced by combining ethine or acetylene with sulphuric acid, and distilling the product with water, just as in the preparation of ethyl alcohol from ethylene:

$$\underset{\text{Sulphuric acid.}}{SO^4HH} + \underset{\text{Ethine.}}{C^2H^2} = \underset{\text{Vinyl-sulphuric acid.}}{SO^4H(C^2H^3)}$$

$$\underset{\text{Vinyl-sulphuric acid.}}{SO^4H(C^2H^3)} + \underset{\text{Water.}}{HOH} = \underset{\text{Sulphuric acid.}}{SO^4HH} + \underset{\text{Vinyl alcohol.}}{C^2H^3(OH)}$$

It is an easily decomposible liquid, having a highly pungent odour, somewhat more volatile than water, soluble in 10 to 15 parts of that liquid, and precipitated from the solution by potassium carbonate. Its chemical reactions have not been much examined, but it is probably an unsaturated secondary alcohol, represented by the formula $\begin{matrix}\cdot\, CH^2\\ |\\ \cdot\, CHOH\end{matrix}$, the dots denoting unsaturated atomicities. It is isomeric with acetic aldehyde and ethylene oxide. The univalent radicle vinyl, C^2H^3, which may be supposed to exist in it, is related to the trivalent radicle ethenyl, in the same manner as allyl to propenyl.

Allyl alcohol, C^3H^6O, is a primary alcohol, yielding acrolein, C^3H^4O, and acrylic acid, $C^3H^4O^2$, by oxidation. It is moreover an unsaturated compound, being capable of taking up 2 atoms of bromine and forming the compound $C^3H^6Br^2O$: hence it may be represented by the formula



$$\begin{matrix} \cdot\,CH^2 \\ | \\ \cdot\,CH \\ | \\ CH^2OH \end{matrix}$$

. All its derivatives are likewise unsaturated compounds, capable of taking up 2 atoms of chlorine, bromine, or other monatomic elements, and passing into glyceryl compounds.

γ. **Monatomic Alcohols.** $C^nH^{2n-2}O$.—Only one alcohol of this series is known, viz. camphol, $C^{10}H^{18}O$; of this however there are four modifications, which appear to be, not metameric, that is to say distinguished by different arrangements of the atoms within the molecule, but only physically isomeric, that is differing from one another by the arrangement of the molecules amongst themselves. They differ in fact by physical, not by chemical characters. One variety, called borneol or Borneo camphor, found in cavities in the trunks of old trees of *Dryabalanops camphora*, has a dextro-gyrate power of 34·4°; a second, produced by the action of alcoholic potash on common camphor, has a dextro-gyrate power of 44·9°; a third, obtained by distilling amber with potash, has a dextro-gyrate power of 45°; and a fourth, called lævo-camphol, found in the alcohol produced in the fermentation of sugar from madder-root, has a lævo-gyrate power of 33·4°, equal and opposite to that of borneol (i. 626, 726).

δ. **Monatomic Alcohols.** $C^nH^{2n-6}O$.—These alcohols are derived from the aromatic hydrocarbons, C^nH^{2n-6}, namely, benzene and its homologues, in the same manner as the fatty alcohols, $C^nH^{2n+2}O$, from the paraffins. The lowest number of the series, corresponding to benzene, C^6H^6, has therefore the composition C^6H^6O or C^6H^5OH. This is the body called *phenol* or *phenyl alcohol*; it is the only alcohol of the series containing 6 atoms of carbon. The higher alcohols of the series admit of isomeric modifications: for every hydrocarbon homologous with benzene may be regarded as a compound of phenyl, C^6H^5, with one or more alcohol-radicles of the series C^nH^{2n+1}, and the formation of an alcohol from such a hydrocarbon by substitution of OH for H may take place either in the phenyl-atom or in one of the alcohol-radicles combined with it: thus from toluene, $C^6H^5.CH^3$, may be obtained the two alcoholic bodies,

$$\underset{\text{Benzyl alcohol,}}{C^6H^5.CH^2OH} \qquad \underset{\text{Cresol;}}{C^6H^4(OH).CH^3}$$

and the higher hydrocarbons of the series are capable of yielding a still greater number of metameric alcoholic compounds. The properties of the compounds thus formed differ considerably accordingly as the hydroxyl is introduced into the phenyl, or into one of the associated alcohol-radicles. The compounds formed in the latter case—benzyl alcohol for example—are true alcohols, analogous in all their reactions to the fatty alcohols; but those in which the hydroxyl replaces a hydrogen atom in the phenyl group possess very different properties, the hydrogen of the hydroxyl being much less readily replaced by other radicles than in their isomerides. These bodies are called by the generic name of phenols. (See Aromatic Series in this volume; also Dictionary, v. 852.)

ε. **Monatomic Alcohols.** $C^nH^{2n-8}O$.—Two only of these bodies are known, viz. cinnyl alcohol, styryl alcohol, or styrone, $C^9H^{10}O$, and cholesterin, $C^{26}H^{44}O$ (i. 925, 992).

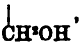
Diatomic Alcohols.

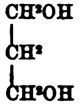
These alcohols are derived from saturated hydrocarbons, by substitution of two equivalents of hydroxyl for two atoms of hydrogen, and may therefore be regarded as compounds of bivalent alcohol-radicles with hydroxyl. Two series of them are known, the first, called glycols, being derived from the paraffins, C^nH^{2n+2}; the second, called diatomic phenols, from the aromatic hydrocarbons, C^nH^{2n-6}.

1. **Glycols.** $C^nH^{2n+2}O^2 = (C^nH^{2n})''\left\{\begin{matrix}OH\\OH\end{matrix}\right.$.—The following table exhibits the names and formulæ of the glycols at present known, together with their boiling points:

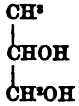
		Boiling point
Ethylene alcohol,	$C^2H^6O^2 = C^2H^4(OH)^2$	197·5°
Propylene alcohol,	$C^3H^8O^2 = C^3H^6(OH)^2$	188°–189°
Butylene alcohol,	$C^4H^{10}O^2 = C^4H^8(OH)^2$	183°–184°
Amylene alcohol,	$C^5H^{12}O^2 = C^5H^{10}(OH)^2$	177°
Hexylene alcohol,	$C^6H^{14}O^2 = C^6H^{12}(OH)^2$	207°
Octylene alcohol,	$C^8H^{18}O^2 = C^8H^{16}(OH)^2$	235°–240°

The glycols are colourless, inodorous, more or less viscid liquids, easily soluble in water and in alcohol; ethylene alcohol is but sparingly soluble in ether, the rest dissolves easily in that liquid.

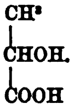
The boiling points of the first four glycols in the table exhibit the singular anomaly of becoming lower as the molecular weight of the compound increases, whereas the six- and eight-carbon glycols have higher boiling points. This anomaly doubtless arises from difference of constitution in the successive terms of the series. Thus ethylene glycol has the constitution  $\begin{array}{l}CH^2OH\\ |\\ CH^2OH\end{array}$, and propylene glycol might be represented by either of the formulæ:

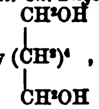


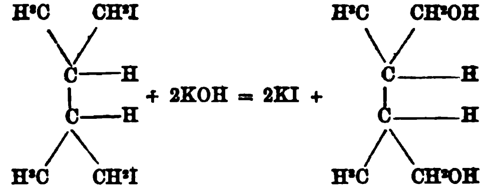
$$\begin{array}{l}CH^2OH\\ |\\ CH^2\\ |\\ CH^2OH\end{array}$$



$$\begin{array}{l}CH^3\\ |\\ CHOH\\ |\\ CH^2OH\end{array}$$

Now the first of these is the true homologue of ethylene glycol; but the actually known propylene glycol appears to have the constitution represented by the second formula, inasmuch as it is converted by oxidation into ordinary lactic acid, which has the constitution  $\begin{array}{l}CH^3\\ |\\ CHOH.\\ |\\ COOH\end{array}$ (See LACTIC ACID.)

Of the six-carbon glycol, $C^6H^{14}O^2$, two modifications have been obtained by Wurtz (*Ann. Ch. Phys.* [4] iii. 122), viz. normal hexylene glycol, $C^6H^{12}(OH)^2$, or probably  $\begin{array}{l}CH^2OH\\ |\\ (CH^2)^4\\ |\\ CH^2OH\end{array}$, produced by combining hexylene, C^6H^{12} (from mannite or from American petroleum), with 2 at. bromine, converting the resulting bromide into an acetate, and distilling this compound with potash; the second, called diallyl-dihydrate or pseudo-hexylene glycol, by distilling diallyl-dihydriodide with potash. (See ALLYL-COMPOUNDS.)



Diallyl-dihydriodide. Diallyl-dihydrate.

or $$(C^6H^{10})^{iv}\left\{\begin{array}{l}H^2\\ I^2\end{array}\right. + 2KOH = 2KI + (C^6H^{10})^{iv}\left\{\begin{array}{l}H^2\\ (OH)^2.\end{array}\right.$$

Both these compounds are syrupy liquids, the first boiling at 207°, or 30° higher than amylene glycol; the second at 215°. When heated with concentrated hydriodic acid, they yield different products, as shown by the following equations:

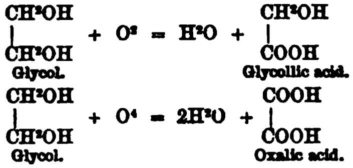
$$C^6H^{12}.(OH)^2 + 3HI = C^6H^{13}.HI + 2H^2O + I^2$$

and

$$C^6H^{10}.H^2(OH)^2 + 2HI = C^6H^{10}.H^2I^2 + 2H^2O.$$

The chemical reactions of the glycols are, for the most part, similar to those of the monatomic alcohols; but inasmuch as the glycols contain 2 atoms of replaceable hydrogen, or of hydroxyl, the reactions generally take place by two stages, yielding two series of products.

1. Ethylene alcohol treated with *nitric acid* gives up 2 or 4 atoms of hydrogen in exchange for oxygen, and is converted into glycollic or oxalic acid, accordingly as the action takes place at ordinary or at higher temperatures:



$$\begin{matrix}CH^2OH\\|\\CH^2OH\end{matrix} + O^2 = H^2O + \begin{matrix}CH^2OH\\|\\COOH\end{matrix}$$

Glycol. Glycollic acid.

$$\begin{matrix}CH^2OH\\|\\CH^2OH\end{matrix} + O^4 = 2H^2O + \begin{matrix}COOH\\|\\COOH\end{matrix}$$

Glycol. Oxalic acid.

Under certain circumstances the corresponding aldehydes are also produced, as glyoxal, $\begin{matrix}COH\\|\\COH\end{matrix}$, from ethylene alcohol, by removal of 4 hydrogen-atoms without substitution.

Propylene glycol, $C^3H^8O^2$, is converted into lactic acid, $C^3H^6O^3$, by oxidation in contact with *platinum black*. When heated with dilute *nitric acid*, it yields glycollic acid, $C^2H^4O^3$, losing carbon as well as hydrogen; and concentrated nitric acid oxidises it still further to oxalic acid. Butylene glycol, $C^4H^{10}O^2$, is converted by slow oxidation with *nitric acid* into oxybutyric acid, $C^4H^8O^3$, and when the action is accelerated by heat, into oxalic acid. Amylene glycol likewise yields oxybutyric acid by slow oxidation with nitric acid.

Other *oxygen-acids* heated with the glycols in closed vessels act upon them in the same manner as on the monatomic alcohols, forming compound ethers, monoacid or diacid according to the proportions used. In the diacid glycol-ethers, the two acid radicles by which the typic hydrogen is replaced may either be the same or different:

$$C^2H^4\left\{\begin{matrix}OH\\OH\end{matrix}\right. + HOC^2H^3O = H^2O + C^2H^4\left\{\begin{matrix}OH\\OC^2H^3O\end{matrix}\right.$$

Ethylene glycol. Acetic acid. Ethylene monoacetate.

$$C^2H^4\left\{\begin{matrix}OH\\OC^2H^3O\end{matrix}\right. + HOC^2H^3O = H^2O + C^2H^4\left\{\begin{matrix}OC^2H^3O\\OC^2H^3O\end{matrix}\right.$$

Monoacetate. Diacetate.

$$C^2H^4\left\{\begin{matrix}OH\\OC^2H^3O\end{matrix}\right. + HOC^4H^7O = H^2O + C^2H^4\left\{\begin{matrix}OC^4H^7O\\OC^2H^3O\end{matrix}\right.$$

Monoacetate. Butyric acid. Butyro-acetate.

The *haloïd acids* act in the same manner, excepting that the reaction never goes beyond the first stage; e.g.,

$$C^2H^4\left\{\begin{matrix}OH\\OH\end{matrix}\right. + HCl = H^2O + C^2H^4\left\{\begin{matrix}Cl\\OH\end{matrix}\right.$$

Ethylene alcohol. Ethylene monochlorohydrate.

The dichlorinated, dibrominated ethers, &c., of the diatomic alcohol-radicles are obtained from the glycols by the action of the chlorides, bromides, and iodides of phosphorus, e.g.,

$$C^2H^4(OH)^2 + 2PCl^5 = 2PCl^3O + 2HCl + C^2H^4Cl^2.$$

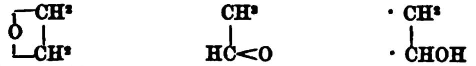
The same compounds are also produced by direct combination of chlorine, bromine and iodine with the olefines.

The monochlorinated, monobrominated ethers, &c., of the glycols, when treated with aqueous alkalis, give up hydrochloric, hydrobromic acid, &c., and leave the oxides of the diatomic alcohols; e.g.,

$$(C^2H^4)''\left\{\begin{matrix}Cl\\OH\end{matrix}\right. = HCl + (C^2H^4)''O$$

Ethylene chlorohydrate. Ethylene oxide.

Ethylene oxide is isomeric with acetic aldehyde and with vinyl alcohol (p. 66).



Ethylene oxide. Aldehyde. Vinyl alcohol.

It is distinguished from aldehyde by its behaviour with ammonia, with which it forms several bases (ii. 587), all of which are syrupy liquids, whereas aldehyde forms with ammonia a crystalline compound not possessing basic properties. A further distinction between these two isomeric bodies is that aldehyde forms crystalline compounds with the acid sulphites of the alkali-metals, a property not possessed by ethylene oxide.

Ethylene oxide is moreover a powerful base, uniting directly with acids to form ethers, and with water to form glycol and the polyethylenic alcohols (ii. 576).

The oxygen-ethers of the higher glycols are not much known, but they appear to be less disposed to combine with water and with acids as their molecules become heavier; thus amylene oxide does not appear to reproduce amylene alcohol by combination with water.

2. **Diatomic Phenols.** $C^nH^{2n-6}O^2$.—There are seven known compounds included in this general formula, viz.,

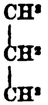
Oxyphenol or Pyrocatechin Resorcin Hydroquinone	$C^6H^6O^2$
Orcin Guaiacol (in part)	$C^7H^8O^2$
Creosol Veratrol Beta-orcin	$C^8H^{10}O^2$

For their characters and modes of formation, see Aromatic Series.

Triatomic Alcohols.

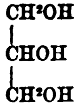
These compounds, of which only a small number have yet been obtained, are derived from saturated hydrocarbons by substitution of 3 equivalents of hydroxyl for 3 at. hydrogen, and may therefore be regarded as compounds of triatomic alcohol-radicles with 3 equivalents of hydroxyl.

Of triatomic alcohols derived from the paraffins, C^nH^{2n+2}, only two are at present known, viz. propenyl alcohol or glycerin, $C^3H^8O^3$, derived from propane or propyl hydride, C^3H^8, and quintenyl alcohol or amyl-glycerin, $C^5H^{12}O^3$, from quintane or amyl hydride, C^5H^{12}.



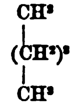
$\begin{array}{c}CH^3\\ |\\ CH^2\\ |\\ CH^3\end{array}$

Propane.



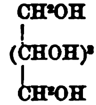
$\begin{array}{c}CH^2OH\\ |\\ CHOH\\ |\\ CH^2OH\end{array}$

Propenyl alcohol.



$\begin{array}{c}CH^3\\ |\\ (CH^2)^3\\ |\\ CH^3\end{array}$

Quintane.



$\begin{array}{c}CH^2OH\\ |\\ (CHOH)^3\\ |\\ CH^2OH\end{array}$

Quintenyl alcohol.

Glycerin is oxidised by strong nitric acid, yielding glyceric acid, $C^3H^6O^4 = CH^2OH.CHOH.COOH$, which is related to glycerin in the same manner as glycollic acid to glycol, or acetic acid to alcohol. The formula of glycerin indicates the possibility of effecting a second substitution of the same kind, which would yield the acid $C^3H^4O^5$; but this acid has not been actually obtained. By a mixture of strong nitric and sulphuric acids, glycerin is converted into the highly explosive compound nitroglycerin, $C^3H^5(NO^2)^3O^3$, which is in reality propenyl trinitrate.

Other oxygen-acids, especially organic acids, heated with glycerin in various proportions, convert it into compound ethers or glycerides, in which 1, 2 or 3 atoms of typic hydrogen are replaced by the radicle of the acid. Hydrochloric and hydrobromic acids act in the same manner, excepting that the reaction always stops at the second stage, just as in the action of these acids upon the glycols it stops at the first stage (p. 69); thus with hydrochloric acid glycerin forms monochlorhydrin, $C^3H^5(OH)^2Cl$, and dichlorhydrin, $C^3H^5(OH)Cl^2$, but not trichlorhydrin, $C^3H^5Cl^3$. The chlorides and bromides of phosphorus act upon glycerin in the same manner as hydrochloric and hydrobromic acids, but their action goes on to the third stage, forming trichlorhydrin and tribromhydrin. Iodide of phosphorus acts in a totally different manner, forming iodopropylene or allyl iodide, C^3H^5I.

The formation and properties of the glycerin-ethers or glycerides, and of the glycidic ethers formed from the chlorhydrins and bromhydrins by abstraction of the elements of hydrochloric or hydrobromic acid, are fully described in the articles Glycerides and Glycidic Ethers (ii. 877, 896).

Polyglycerins, analogous to the polyethylenic alcohols, and consisting of two or more molecules of glycerin united into a single molecule, with elimination of a number of water-molecules less by one than the number of glycerin-molecules which combine together, have also been described (ii. 894). Their constitution may be represented by the following general equation:

$$nC^3H^5(OH)^3 - (n-1)H^2O = (C^3H^5)^n\left\{\begin{matrix}O^{n-1}\\(OH)^{n+2}\end{matrix}\right.$$

The atomicity of the resulting polyglycerin (determined by the number of equivalents of hydroxyl contained in it) is $n + 2$.

Quintenyl alcohol or **Amyl glycerin**, $C^5H^{12}O^3 = (C^5H^9)'''(OH)^3$, is formed from dibromide of bromoquintene or bromamylene, $C^5H^9Br.Br^2$, or quintenyl bromide, $C^5H^9Br^3$, by the series of processes represented in the following equations:

$$\begin{array}{ccccccc}C^5H^9Br^3 & + & 2AgOC^2H^3O & = & 2AgBr & + & (C^5H^9)'''\left\{\begin{matrix}(OC^2H^3O)^2\\Br\end{matrix}\right.\\ \text{Quintenyl bromide.} & & \text{Silver acetate.} & & \text{Silver bromide.} & & \text{Quintenyl diaceto-bromhydrin.}\end{array}$$

$$\begin{array}{ccccccc}(C^5H^9)'''\left\{\begin{matrix}(OC^2H^3O)^2\\Br\end{matrix}\right. & + & 2KOH & = & 2KOC^2H^3O & + & (C^5H^9)'''\left\{\begin{matrix}(OH)^2\\Br\end{matrix}\right.\\ \text{Quintenyl diaceto-bromhydrin.} & & \text{Potassium hydrate.} & & \text{Potassium acetate.} & & \text{Quintenyl bromhydrin.}\end{array}$$

$$\begin{array}{ccccccc}(C^5H^9)'''\left\{\begin{matrix}(OH)^2\\Br\end{matrix}\right. & + & KOH & = & KBr & + & (C^5H^9)'''(OH)^3\\ \text{Quintenyl bromhydrin.} & & & & & & \text{Quintenyl alcohol.}\end{array}$$

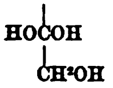
Quintenyl alcohol is a thick colourless liquid, having a sweet aromatic taste, and soluble in water (Bauer, *Zeitschrift für Chem. u. Pharm.* 1861, p. 673).

Triatomic Phenols. $C^nH^{2n-6}O^3$.—There are three compounds represented by the formula $C^6H^6O^3$, and exhibiting a certain relationship to the phenols; these are: 1. **Pyrogallol** or **pyrogallic acid**, formed from gallic (dioxysalicylic) acid, in the same manner as oxyphenol from oxysalicylic acid and phenol from salicylic acid: $C^7H^6O^5 = CO^2 + C^6H^6O^3$; 2. **Phloroglucin**, produced from phlorizin, a crystalline substance existing in the root-bark of the apple, pear, plum and cherry trees; and 3. **Frangulin**, a yellow crystallisable substance existing in the bark of *Rhamnus frangula* (ii. 706). The last two form explosive substitution-products with nitric acid; phlorizin and pyrogallol form substitution-products with bromine.

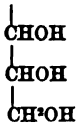
TETRATOMIC ALCOHOLS.

The only tetratomic alcohols at present known are **erythrite**, **erythromannite**, or **phycite**, $C^4H^{10}O^4 = (C^4H^6)^{iv}(OH)^4$, a saccharine substance existing in *Protococcus vulgaris* (iv. 504); and **propylphycite** or **trityl-phycite**, $C^3H^8O^4 = (C^3H^4)^{iv}(OH)^4$, produced by combining epichlorhydrin, C^3H^5OCl, with hypochlorous acid, $HClO$, treating the resulting dichlorhydrin of propylphycite, $(C^3H^4)^{iv}Cl^2(OH)^2$, with silver acetate, whereby it is converted into the corresponding diacetin, $(C^3H^4)^{iv}(OC^2H^3O)^2(OH)^2$, and heating this diacetin with aqueous potash (v. 893).

These two alcohols are of decidedly saccharine character, and form explosive nitro-compounds. They contain 4 atoms of hydrogen, replaceable by acid or alcoholic radicles, so as to form ethers; but two of these hydrogen-atoms are more easily replaceable than the other two, probably those which in the following formulæ are contained in the hydroxyl belonging to the two groups CH^2OH:



Propylphycite.



Erythrite.

Hexacid ethers of these acids are also formed by combination of the tetracid ethers with two molecules of free acid, e.g. erythritic hexbenzoate

$$= (C^4H^6)^{iv}(C^7H^5O^2)^4.2C^7H^6O^2.$$

PENTATOMIC ALCOHOLS.

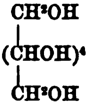
Pinite and **quercite**, two saccharine bodies having the composition $C^6H^{12}O^5$, probably belong to this class of bodies, inasmuch as they form ethers when treated with acids, and the atomicity of an alcohol is equal to the number of oxygen-atoms which it contains. Pinite forms two benzoic ethers, viz. $C^6H^7(OC^7H^5O)^2(OH)^3$ and $C^6H^7(OC^7H^5O)^4(OH)$.

HEXATOMIC ALCOHOLS.

This class of compounds includes most of the saccharine substances found in plants, and others produced from them by artificial transformation. Two of the natural sugars, **mannite** and **dulcite**, having the composition $C^6H^{14}O^6$ or $(C^6H^8)^{vi}(OH)^6$, are saturated hexatomic alcohols derived from the saturated hydrocarbon, C^6H^{14}. Several others, called **glucoses**, contain $C^6H^{12}O^6$; that is to say, 2 atoms of hydrogen less than mannite and dulcite, and may therefore be regarded—so far as composition is concerned—as the aldehydes of these alcohols; ordinary glucose (grape-sugar) is, in fact, converted into mannite by the action of nascent hydrogen, just as acetic aldehyde, C^2H^4O, is converted into common alcohol, C^2H^6O. Further, there are **diglucosic alcohols**, $C^{12}H^{22}O^{11}(= 2C^6H^{12}O^6 - H^2O)$, related to the glucoses in the same manner as diethylene-alcohol to glycol, or diglycerin to glycerin: the most important of these are **cane-sugar** and **milk-sugar**; and, lastly, there are certain vegetable products—viz. **starch**, **cellulose**, and a few others, represented by the formula $nC^6H^{10}O^5$ (mostly $C^{18}H^{30}O^{15}$)—which may be regarded as the oxygen-ethers or anhydrides of the glucoses, or rather of polyglucosic alcohols, from which indeed they differ by the elements of a molecule of water.

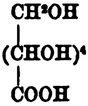
Mannite, $C^6H^{14}O^6 = (C^6H^8)^{vi}(OH)^6$, the essential constituent of manna, is formed artificially by treating a solution of glucose with sodium amalgam, $C^6H^{12}O^6 + H^2 = C^6H^{14}O^6$. The same transformation of glucose takes place under the influence of certain ferments.

By oxidation with platinum-black, mannite is converted into mannitic acid, $C^6H^{12}O^7$, and mannitose, $C^6H^{12}O^6$, a sugar isomeric with glucose; and by oxidation with nitric acid, into saccharic acid, $C^6H^{10}O^8$, and finally into oxalic acid. Mannitic and saccharic acids are related to mannite in the same manner as glycollic and oxalic acids to glycol, as shown by the following formulæ:



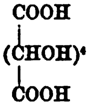
$$\begin{matrix} CH^2OH \\ | \\ (CHOH)^4 \\ | \\ CH^2OH \end{matrix}$$

Mannite.



$$\begin{matrix} CH^2OH \\ | \\ (CHOH)^4 \\ | \\ COOH \end{matrix}$$

Mannitic acid.



$$\begin{matrix} COOH \\ | \\ (CHOH)^4 \\ | \\ COOH \end{matrix}$$

Saccharic acid.

For the other reactions of mannite, see vol. iii. p. 823.

Dulcite, obtained from *Melampyrum nemorosum*, and from a crystalline substance of unknown origin imported from Madagascar, resembles mannite in most of its chemical relations, but differs from it in solubility, in crystalline form, and in yielding by oxidation with nitric acid, not saccharic acid, but the isomeric compound **mucic acid**.

Isodulcite, a saccharine substance obtained, according to Hlasiwetz and Pfaundler (v. 465), by the action of dilute acid on quercitrin, forms large crystals having the same composition as mannite and dulcite, but giving off 1 molecule of water at 105°–110°.

With fuming nitric acid, all three of these substances yield nitric ethers of a more or less explosive character. *Nitromannite*, $C^6H^8(NO^2)^6O^6$, explodes violently by percussion, or when suddenly heated; *hexnitrodulcite*, $C^6H^8(NO^2)^6O^6$, gives off nitrous fumes when heated, but does not explode, and is slowly converted at ordinary temperatures into *tetra-nitrodulcite*, $C^6H^{10}(NO^2)^4O^6$. *Nitro-isodulcite*, $C^6H^{11}(NO^2)^3O^5$, is slightly explosive.

The glucoses $C^6H^{12}O^6$, as already observed, are related in composition to the saturated hexatomic alcohols in the same manner as aldehydes to alcohols, and may be converted into the saturated alcohols by the action of nascent hydrogen. But they exhibit the characteristic property of alcohols, in forming ethers by combination with acids and elimination of water. They are at once poly-alcohols and aldehydes, just as lactic acid is half alcohol and half acid. The following varieties of glucose are known:

1. *Ordinary glucose*, produced by hydration of starch under the influence of dilute

acids or of diastase, and existing ready-formed, together with other kinds of sugar, in honey and various fruits, especially in grapes, and alone in diabetic urine.

2. *Maltose*, produced by the limited action of diastase on starch, and differing from glucose only in its optical rotatory power.

3. *Levulose*, existing in cane-sugar which has been acted upon by acids, and obtained pure by the action of dilute acids upon the variety of starch called inulin.

4. *Mannitose*, produced by oxidation of mannite.

5. *Galactose*, formed by the action of acids on milk-sugar.

6. *Inosite*, existing in muscular flesh.

7. *Sorbin*, obtained from mountain-ash berries.

8. *Eucalyn*, existing, together with another kind of sugar, in the so-called Australian manna.

The first four of these glucoses exhibit but very slight diversity in their chemical properties, differing chiefly indeed in their action on polarised light, and a few other physical properties. They all yield saccharic acid by oxidation. Galactose differs from them in yielding mucic acid when oxidised. Inosite, sorbin, and eucalyn exhibit still greater differences in their chemical properties, especially in not being fermentable except under very peculiar circumstances, whereas the five other glucoses undergo vinous fermentation when placed under certain conditions in contact with yeast.

All the glucoses, except inosite, are decomposed by boiling with aqueous alkalis; this property distinguishes them from mannite and dulcite. They are not carbonised by strong sulphuric acid at ordinary temperatures. When boiled with a solution of potassio-cupric tartrate, they throw down the copper in the form of red cuprous oxide.

Glucosates or *Glucosides.*—When ordinary glucose is heated to 100°–120° for fifty or sixty hours with acetic, butyric, stearic, benzoic, and other organic acids, the two unite, with elimination of water, and compound-ethers called glucosates are formed, analogous to the mannitanates. A number of these artificial glucosates have been prepared by Berthelot, who regards them as derivatives of *glucosan*, $C^6H^{10}O^5$, because when heated with alkalis they yield glucosan, not glucose. Thus, there is a glucoso-butyric ether to which Berthelot assigns the formula $C^6H^8(C^4H^7O)^2O^5$, and an acetic ether, which he regards as hexaceto-glucosan, $C^6H^4(C^2H^3O)^6O^5$; but they are merely oily liquids which are very difficult to obtain pure, and therefore their analyses are not much to be depended on.

The natural glucosates, many of which constitute the neutral bitter principles of the vegetable kingdom, have a similar constitution. None of them have been prepared artificially; but they are all resolved by boiling with dilute acids into glucose and some other compound (see vol. pp. 865-872).

The polyglucosic alcohols, including cane-sugar and other bodies more or less resembling it, may be regarded as formed by the combination of two or more molecules of glucose, with elimination of a number of water-molecules less by one than the number of glucose molecules which enter into the combination; thus:

$$\begin{array}{llrcl} & 2C^6H^{12}O^6 & - \quad H^2O & = & C^{12}H^{22}O^{11}, \text{ Diglucosic alcohol.} \\ & 3C^6H^{12}O^6 & - \quad 2H^2O & = & C^{18}H^{32}O^{16}, \text{ Triglucosic alcohol.} \\ \text{generally:} & nC^6H^{12}O^6 & - (n-1)H^2O & = & C^{6n}H^{2(5n+1)}O^{5n+1}. \end{array}$$

The only known alcohols of this group are diglucosic alcohols, $C^{12}H^{22}O^{11}$; but starch, cellulose, and other neutral plant-constituents may be regarded as the oxygen-ethers or anhydrides of polyglucosic alcohols of higher orders.

The known diglucosic alcohols are the following:

1. *Cane-sugar* or *saccharose*, widely diffused in the vegetable kingdom, and existing in particular abundance in the sugar-cane and in beet-root.

2. *Parasaccharose*, produced, according to Jodin (v. 473), by a peculiar spontaneous fermentation of cane-sugar.

3. *Melitose*, from the manna of various species of Eucalyptus.

4. *Melezitose*, from the manna of *Larix europæa.*

5. *Trehalose*, from Trehala manna, and from a species of Echinops growing in the East; and *Mycose*, perhaps identical with it, from ergot of rye.

6. *Milk-sugar*, *lactin*, or *lactose*, from milk.

7. *Gum*, a widely diffused constituent of plants, exhibiting several varieties, which differ considerably in physical properties, solubility, &c.

The anhydrides of the polyglucosic alcohols, derived from these compounds by elimination of a single molecule of water, are all polymeric one with another, as shown by the following equations:

$$\underset{\text{Glucose.}}{C^6H^{12}O^6} - H^2O = C^6H^{10}O^5$$

$$\underset{\text{Diglucosic alcohol.}}{C^{12}H^{22}O^{11}} - H^2O = 2C^6H^{10}O^5$$

$$\underset{\text{Triglucosic alcohol.}}{C^{18}H^{32}O^{16}} - H^2O = 3C^6H^{10}O^5$$

generally: $C^{6n}H^{2(5n+1)}O^{5n+1} - H^2O = nC^6H^{10}O^5$.

The known bodies of this group are starch, dextrin, cellulose, inulin from dahlia tubers, and glycogen, obtained from the livers of animals, and entering largely into the composition of most of the tissues of the embryo (ii. 906).

Starch and cellulose appear to consist of $C^{18}H^{30}O^{15}$. That such is the molecular formula of starch appears from the manner in which that substance is converted into dextrin and glucose by the action of dilute acids or of diastase. It was formerly supposed that, in the action of acids or of diastase upon starch, the starch is first converted into dextrin by a mere alteration of physical structure, and that the dextrin then takes up the elements of water, and is converted into glucose, this second stage of the process occupying a much longer time than the first; but from recent experiments by Musculus (*Comptes rendus*, l. 785; liv. 194; *Ann. Ch. Phys.* [3] lx. 208; [4] vi. 177), it appears that both dextrin and glucose are produced at the very commencement of the reaction, and always in the proportion of 1 molecule of glucose to 2 molecules of dextrin, whence it may be inferred that the molecule of starch contains $C^{18}H^{30}O^{15}$, and that it is resolved into glucose and dextrin by taking up a molecule of water:

$$\underset{\text{Starch.}}{C^{18}H^{30}O^{15}} + H^2O = \underset{\text{Glucose.}}{C^6H^{12}O^6} + \underset{\text{Dextrin.}}{2C^6H^{10}O^5}$$

When the conversion is effected by a dilute acid, the dextrin is, after several hours' boiling, completely converted into glucose, which is therefore the sole ultimate product of the reaction. But when diastase is used as the converting agent, the production of glucose goes on only so long as there is any unaltered starch still present, the dextrin undergoing no further alteration.

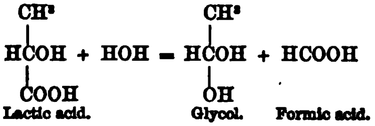
That cellulose consists also of $C^{18}H^{30}O^{15}$ appears from the substitution-products (pyroxylins) which it yields under the influence of strong nitric acid and a mixture of nitric and sulphuric acids, these products being represented (according to Hadow's results) by the formulæ: $C^{18}H^{23}(NO^2)^7O^{15}$ (cotton-xyloïdin); $C^{18}H^{22}(NO^2)^8O^{15}$; and $C^{18}H^{21}(NO^2)^9O^{15}$ or $C^6H^7(NO^2)^3O^5$ (trinitrocellulose or gun-cotton). See PYROXYLIN (iv. 777).

ALCOSOL. The gelatinous compound of alcohol with colloïdal silicic acid (see COLLOÏDAL ACIDS, in Appendix, vol. v. p. 1089).

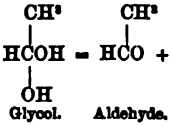
ALDEHYDE. C^2H^4O.—Produced: *α*. By heating ethylene bromide with water to 150°–160° in a sealed tube (Carius, *Ann. Ch. Pharm.* cxxxi. 172):

$$C^2H^4Br^2 + H^2O = 2HBr + C^2H^4O.$$

β. When aqueous ethylamine is poured upon crystallised potassium permanganate (Carstangen, *J. pr. Chem.* lxxxix. 486).—*γ*. By the action of a powerful electric current on a mixture of 100 pts. absolute alcohol and 1 pt. strong sulphuric acid or 1 pt. potassium hydrate, hydrogen being at the same time evolved at the negative pole: $C^2H^6O = C^2H^4O + H^2$ (Jaillard, *Compt. rend.* lviii. 1203).—*δ*. Together with fórmic acid, by heating fermentation lactic acid for several hours to 130° with dilute sulphuric acid, the reaction probably taking place by the following two stages:

(1). 

$$\underset{\text{Lactic acid.}}{\begin{array}{c}CH^3\\ |\\ HCOH\\ |\\ COOH\end{array}} + HOH = \underset{\text{Glycol.}}{\begin{array}{c}CH^3\\ |\\ HCOH\\ |\\ OH\end{array}} + \underset{\text{Formic acid.}}{HCOOH}$$

(2). 

$$\underset{\text{Glycol.}}{\begin{array}{c}CH^3\\ |\\ HCOH\\ |\\ OH\end{array}} = \underset{\text{Aldehyde.}}{\begin{array}{c}CH^3\\ |\\ HCO\end{array}} + HOH$$

(Erlenmeyer, *Zeitschr. f. Chem.* [2] iv. 343).

Pure aldehyde heated to 160° for a hundred hours in a sealed tube is resolved, without formation of gas, into water, and a resinous product which is a mixture of hydrocarbons polymeric with acetylene. A small quantity of alcohol is formed at the same time, together with an acid, probably acetic acid: $2C^2H^4O + H^2O = C^2H^6O + C^2H^4O^2$ (Berthelot, *Compt. rend.* lvi. 703).

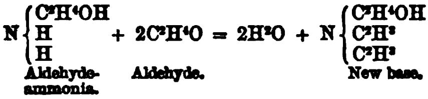
Vapour of aldehyde passed over heated quicklime yields, together with gases, a liquid distillate, consisting of acetone and other ketones richer in carbon (Schlœmilch, *Zeitschr. f. Chem.* [2] v. 336).

Aldehyde treated with *hydriodic acid* at high temperatures yields ethane, C^2H^6, together with water and free iodine: $C^2H^4O + 4HI = C^2H^6 + H^2O + 2I^2$ (Berthelot, *Bull. Soc. Chim.* [2] vii. 59).

Aldehyde exposed for six months to the action of a solution of *ammonia* in absolute alcohol forms a brownish liquid, which when distilled gives off ammonia and a volatile base, C^6H^9N. The residue is resinous, and when purified forms a yellow powder which combines with acids, and has the composition of triethylene-diamine, $N^2(C^2H^4)^3$. It is decomposed by water and acids, in the manner represented by the equation:

$$C^6H^{12}N^2.2HCl + H^2O = NH^4Cl + C^6H^{11}NO.HCl.$$

The new base, $C^6H^{11}NO$, which is amorphous, yellow, and soluble in water, is a tertiary monamine, and is likewise formed when an alcoholic solution of aldehyde-ammonia containing excess of aldehyde is exposed to a temperature of 50°–60°:



$$N\begin{cases}C^2H^4OH\\H\\H\end{cases} + 2C^2H^4O = 2H^2O + N\begin{cases}C^2H^4OH\\C^2H^3\\C^2H^3\end{cases}$$

Aldehyde-ammonia. Aldehyde. New base.

When aldehyde is decomposed by ammonia at 100°, two other bases are formed, viz. $C^{10}H^{15}NO$ and $C^8H^{13}NO$, which are probably constituted similarly to the base $C^6H^{11}NO$ (H. Schiff, *Bull. Soc. Chim.* [2] viii. 443).

Aldehyde heated to 100° with strong solutions of certain *neutral salts*, as formate or acetate of potassium, is converted into vinyl oxide, $C^4H^6O = 2C^2H^4O - H^2O$ (Lieben, *Rép. Chim. pure*, 1861, p. 190).

Aldehyde (2 mol.) treated with *ammonium suphocarbamate* (1 mol.) is converted into water and carbothialdine:

$$2C^2H^4O + CH^2(NH^4)NS^2 = 2H^2O + C^5H^{10}N^2S^2.$$

(E. Mulder, *J. pr. Chem.* ciii. 178).

Aldehyde mixed with water and saturated with *cyanogen* deposits crystals of oxamide, the mother-liquor retaining a compound of aldehyde and oxamide, which is decomposed by ebullition, the aldehyde distilling over slowly, and crystals of oxamide being deposited (Liebig, *Ann. Ch. Pharm.* cxiii. 360). According to Berthelot, a. Péan de St. Gilles (*Bull. Soc. Chim.* 1863, p. 502), cyanogen gas passed into crude aldehyde forms a white precipitate, $C^6H^{10}N^4O^4$, which contains the elements of cyanogen, water, and aldehyde, $(4CN + 3H^2O + C^2H^4O)$, or of aldehyde and oxamide, with elimination of water, $C^6H^{10}N^4O^4 = C^2H^4O.2C^2H^4N^2O^2 - H^2O$. Aldehyde dissolves *cyanamide*, and the mixture after 24 hours, changes into a body resembling copal resin, soluble in alcohol, and precipitated therefrom in white flocks by ether. This compound contains $N^2C^6H^{14}O$ (Knop, *Ann. Ch. Pharm.* cxxx. 253). When a mixture of aldehyde, hydrocyanic acid, and hydrochloric acid is left to itself, lactic acid is produced, together with a small quantity of formic acid:

$$C^2H^4O + CHN + HCl + 2H^2O = NH^4Cl + C^3H^6O^3$$

(Wislicenus. *Ann. Ch. Pharm.* cxxviii. 1).

A compound of aldehyde with *mercurous bromide*, $C^2H^4O.Hg^2Br^2$, is obtained by heating vinyl bromide (monobromethylene) with mercuric acetate to 100°:

$$2C^2H^3Br + 2(C^2H^3O^2)^2Hg + 4H^2O = C^2H^4O.Hg^2Br^2 + 5C^2H^4O^2 + H^2O.$$

The compound separates as a white amorphous precipitate, which turns brown in the air, with evolution of aldehyde (Saytzeff a. Glinsky, *Zeitschr. f. Chem.* [2] iii. 675).

Hydrocyanide of Aldehyde. $CNH.C^2H^4O$.—Aldehyde and hydrocyanic acid, both anhydrous, if mixed in molecular proportion, unite in the course of 8 or 10 days, forming a liquid the greater part of which distils between 171° and 185°, the portion of constant boiling point distilling between 182° and 184°. On attempting to fractionate this product, it splits up into its components, a considerable portion distilling between 40° and 60°; but if the distillate be left to itself, the two bodies reunite and reproduce the compound distilling at 184°.

Hydrocyanide of aldehyde is a colourless oily liquid, having a bitter acrid taste, and smelling somewhat like its components; it becomes syrupy at – 21°. Its decomposition by heat is accelerated by *potash*, the products then formed being potassium cyanide and rosin of aldehyde. It absorbs *ammonia gas* at – 10°, forming a basic compound which yields a crystalline hydrochloride and platinochloride. Aqueous ammonia appears to act in the same manner.

Hydrochloric acid in strong aqueous solution acts violently on aldehyde-hydrocyanide at ordinary temperatures, but the two liquids may be mixed quietly below 0°, and the liquid if then left to get gradually warm is resolved into sal-ammoniac, which crystallises out, and lactic acid, which remains in the liquid state:

$$\mathrm{C^2H^4O.CNH + HCl + 2H^2O = NH^4Cl + C^3H^6O^3}.$$

The reactions with potash and with hydrochloric acid show that the compound is not identical, but only isomeric, with glycolic monocyanhydrin (Maxwell Simpson a. Gautier, *Bull. Soc. Chim.* [2] viii. 277).

Polymeric Modifications of Aldehyde.—Acraldehyde, $\mathrm{C^4H^8O^2}$, first observed by Wurtz, is produced, together with aldehyde, by the action of zinc chloride on glycol. On treating the resulting liquid with calcium chloride, acraldehyde separates as a liquid lighter than water, and having a pungent odour. It is soluble in all proportions in water, alcohol, and ether, and reduces an ammoniacal solution of silver nitrate. It boils at 110°, and has a vapour-density of 2·877, which is nearly double that of aldehyde (Bauer, *Rép. Chim. pure*, 1868, p. 294).

The solid modifications, elaldehyde and metaldehyde, are described in vol. i. p. 109; the liquid modification, paraldehyde, in vol. iv. p. 349.

Chloraldehydes. *Monochloraldehyde*, $\mathrm{C^2H^3ClO}$, is produced by passing vinyl chloride into well-cooled hypochlorous acid. It is a neutral, oily, easily decomposible liquid, which on exposure to the air is converted into chloracetic acid (Saytzeff a. Glinsky, *Zeitschr. f. Chem.* [2] iii. 675). On leaving it to stand at a lower temperature, in a well-stopped flask in contact with hypochlorous acid and excess of mercuric oxide, a crystalline crust is formed at the bottom of the vessel, consisting of a compound of chloraldehyde with calomel, $\mathrm{C^2H^3ClO.Hg^2Cl^2}$. This compound melts at 96° to a transparent mass, gradually changing to a crystalline powder. In cold aqueous solution it is slowly resolved into calomel and chloraldehyde. Hydrogen sulphide decomposes it immediately, precipitating the mercury, and setting the chloraldehyde free. Mixed in aqueous solution with iodide or cyanide of potassium, it is converted into iodaldehyde or cyanaldehyde (Glinsky, *ibid.* iv. 617).

Vinyl bromide passed into cold aqueous hypochlorous acid forms an easily soluble product, not volatile without decomposition, and probably consisting of a mixture of chloraldehyde and bromaldehyde (Saytzeff a. Glinsky).

Dichloraldehyde. $\mathrm{C^2H^2Cl^2O}$ (E. Paterno, *Giornale di Scienze nat. ed econom. di Palermo*, v. 123, 127).—Produced by distilling dichloracetal with 4 to 6 vols. sulphuric acid in an oil-bath heated to 130°. On rectifying the distillate, the dichloraldehyde passes over at 88°–90°. It is a liquid which boils at 89°–90°, attracts moisture from the air, and is thereby converted into a hydrate crystallising in beautiful laminæ. Left to itself, even in sealed tubes, it becomes dense, and changes into a white amorphous mass, which has the aspect of porcelain, but when heated to 120° is reconverted into the original product. Dichlorinated aldehyde dissolves without decomposition in alcohol and ether; when poured into water it first sinks to the bottom, and then dissolves, especially on application of heat; in short, it exhibits the most complete analogy with chloral. It is difficult to oxidise, its vapour not undergoing any sensible alteration when mixed with air or oxygen and passed over red-hot spongy platinum; but when gently heated with several times its own volume of fuming nitric acid, it is energetically attacked and converted into *dichloracetic acid*, $\mathrm{C^2H^2Cl^2O^2}$. Phosphorus pentachloride attacks it strongly, producing the compound $\mathrm{C^4H^4Cl^6O}$ or $\mathrm{C^2H^2Cl^2O.C^2H^2Cl^4}$, the action doubtless consisting in the replacement of O by $\mathrm{Cl^2}$ (as in the action of $\mathrm{PCl^5}$ on aldehydes in general), whereby $\mathrm{C^2H^2Cl^4}$ is produced, which, as soon as it is formed, unites with a portion of the undecomposed dichlorinated aldehyde, producing the compound $\mathrm{C^4H^4Cl^6O}$. The constitution of this body may be represented by the following formula:

$$\mathrm{CHCl^2-CH^2-O-CCl^2-CHCl^2},$$

or perhaps by

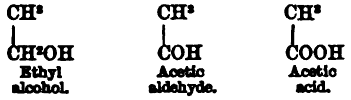
$$CHCl^2 - CHCl - O - CHCl - CHCl^2.$$

The compound $C^4H^4Cl^6O$ is a colourless oil, having an irritating odour, heavier than water, soluble in alcohol and ether; it distils at 250°, emitting acid vapours. Alcoholic potash attacks it strongly, with evolution of heat and formation of potassium chloride; and on adding water to the resulting liquid, a heavy aromatic oil separates, boiling at 196°, and having the composition $C^4H^2Cl^4O$, that is to say, containing 2HCl less than the preceding. This last compound unites directly with 4 at. bromine, forming the crystalline compound $C^4H^2Cl^4Br^4O$. In this respect the compound $C^4H^2Cl^4O$ is analogous to Malaguti's *chloroxëthose*, C^4H^6O, which he obtained by abstracting 4 at. chlorine from perchlorinated ethylic oxide, $C^4Cl^{10}O$ (i. 924). According to this analogy, the compound $C^4H^4Cl^6O$ may be designated as *hexchlorinated ethylic oxide*, and $C^4H^2Cl^4Br^4O$ as *tetrachloro-tetrabrominated ethylic oxide*. The two compounds C^4Cl^6O and $C^4H^2Cl^4O$ may also be regarded respectively as *perchlorinated vinyl oxide*, $\left.\begin{matrix}C^2Cl^3\\C^2Cl^3\end{matrix}\right\}O$, and *tetrachlorinated vinyl oxide*.

Iodaldehyde, C^2H^3IO, is produced by boiling the aqueous solution of monochloraldehyde with potassium iodide, and may be dissolved out by ether from the solution, after the latter has been left to itself for about twelve hours. On evaporating the ether, iodaldehyde remains as a liquid, which at first is tolerably mobile, and has a faint odour like that of aldehyde, but after a while becomes thicker and acquires a stronger odour. It is decomposed by distillation, giving off aldehyde and its polymerides, and leaving a residue chiefly consisting of iodine. A similar decomposition takes place when the aqueous solution is heated. When oxidised in ethereal solution, with a few drops of fuming nitric acid, it is converted into iodacetic acid, $C^2H^3IO^2$ (Glinsky, *Zeitschr. f. Chem.* [2] iv. 618).

Cyanaldehyde, $C^2H^3(CN)O$, separates in heavy oily drops on adding potassium cyanide to an aqueous solution of monochloraldehyde. It is sparingly soluble in water; decomposes easily in the moist state and in aqueous solution; cannot be distilled; does not unite with sodium bisulphite. By oxidation with nitric acid it is converted into cyanacetic acid (Glinsky).

ALDEHYDES. These bodies are derived from alcohols by elimination of one or more molecules of hydrogen, (H²), without the introduction of an equivalent quantity of oxygen, so that they hold a position intermediate between the alcohols and the acids; e.g.,



$$\begin{array}{ccc} CH^3 & CH^3 & CH^3 \\ | & | & | \\ CH^2OH & COH & COOH \\ \text{Ethyl alcohol.} & \text{Acetic aldehyde.} & \text{Acetic acid.} \end{array}$$

The hydrogen eliminated in the conversion of an alcohol into an aldehyde is that which is in immediate connection with the hydroxyl, or which belongs to the group CH^2OH; consequently a monatomic alcohol can yield but one aldehyde; but a diatomic alcohol may yield two, by removal of H² and of 2H²; a triatomic alcohol three, and so on. At present, however, we are acquainted only with aldehydes derived from monatomic and diatomic alcohols, and even among these it is only the series of aldehydes derived from the monatomic alcohols of the series $C^nH^{2n+2}O$ and $C^nH^{2n-6}O$ that exhibit any approach to completeness.

The statement in vol. i. p. 110, that monatomic aldehydes are the ethers of diatomic alcohols, was founded on observations which subsequent investigation has shown to be inexact; the aldehydes are isomeric, not identical, with the ethers of diatomic alcohols.

To the list of monatomic aldehydes, $C^nH^{2n}O$, corresponding to the fatty acids, must now be added the first of the series, namely, formic aldehyde, CH^2O, recently discovered by Hofmann (*Proc. Roy. Soc.* xvi. 156). It is produced when a current of air, charged with vapour of methyl alcohol, is directed upon an incandescent spiral of platinum wire; by suitable condensing arrangements, a liquid may be obtained consisting of a solution of the aldehyde in methyl alcohol. This liquid, rendered slightly alkaline by ammonia, and gently warmed with silver nitrate, yields a beautiful specular deposit of silver, with greater ease even than ordinary acetic aldehyde. The same solution, heated with a few drops of caustic potash, deposits drops of a brownish oil, having the odour of the resin of acetic aldehyde.

Formic aldehyde has not yet been obtained in the pure state; but by treating its solution with hydrogen sulphide, and heating the resulting liquid with strong hydrochloric acid, it solidifies, on cooling, to a dazzling white mass of felted needles, consisting of the corresponding sulphur-compound, CH^2S.

To the list of aromatic aldehydes, $C^nH^{2n-8}O$, must be added toluic aldehyde, $C^7H^6O = C^6H^5.CHO$, produced by distilling a mixture of the calcium-salts of toluic and formic acids (v. 864); and sycocerylic aldehyde, $C^{18}H^{28}O$, which appears to be formed by oxidation of sycocerylic alcohol (v. 646).

Reactions of Aldehydes.—The following reactions, in addition to those mentioned in vol. i., are common to all the monatomic aldehydes.

1. By fusion with *potassium hydrate*, they are converted into the corresponding acids, with evolution of hydrogen:

$$\underset{\text{Acetic aldehyde.}}{C^2H^4O} + KOH = \underset{\text{Potassium acetate.}}{C^2H^3KO^2} + H^2$$

$$\underset{\text{Benzoic aldehyde.}}{C^7H^6O} + KOH = \underset{\text{Potassium benzoate.}}{C^7H^5KO^2} + H^2$$

2. *Nascent hydrogen*, evolved by the action of water on sodium amalgam, converts them into the corresponding alcohols; e.g., $C^2H^4O + H^2 = C^2H^6O$. If, however, the aldehyde belongs to a non-saturated series, the action goes further, an additional quantity of hydrogen being taken up, whereby the alcohol first formed is converted into a saturated alcohol belonging to another series; thus:

$$\underset{\text{Acrylic aldehyde.}}{C^3H^4O} + H^2 = \underset{\text{Allyl alcohol.}}{C^3H^6O}$$

and

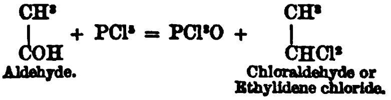
$$\underset{\text{Allyl alcohol.}}{C^3H^6O} + H^2 = \underset{\text{Propyl alcohol.}}{C^3H^8O}$$

Nascent hydrogen evolved by the action of zinc on sulphuric acid does not appear to unite with aldehydes.

Benzoic aldehyde, under the influence of nascent hydrogen evolved by the action of zinc on hydrochloric acid, doubles its molecule and takes up 2 at. of hydrogen:

$$\underset{\text{Benzoic aldehyde.}}{2C^7H^6O} + H^2 = \underset{\text{Hydro-benzoin.}}{C^{14}H^{14}O^2}$$

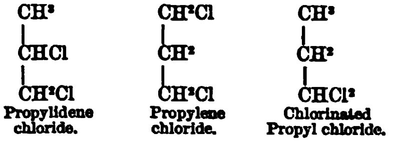
3. *Phosphorus pentachloride* converts aldehydes into chloraldehydes, compounds derived from aldehydes by substitution of Cl^2 for O; thus:



$$\begin{array}{c}CH^3\\|\\COH\end{array} + PCl^5 = PCl^3O + \begin{array}{c}CH^3\\|\\CHCl^2\end{array}$$

Aldehyde. Chloraldehyde or Ethylidene chloride.

The compounds thus produced are isomeric with the chlorides of the olefines, and with the monochlorinated chlorides of the corresponding monatomic alcohols; e.g.,



$$\begin{array}{c}CH^3\\|\\CHCl\\|\\CH^2Cl\end{array} \qquad \begin{array}{c}CH^2Cl\\|\\CH^2\\|\\CH^2Cl\end{array} \qquad \begin{array}{c}CH^3\\|\\CH^2\\|\\CHCl^2\end{array}$$

Propylidene chloride. Propylene chloride. Chlorinated Propyl chloride.

Ethylidene chloride, $CH^3.CHCl^2$, is *identical* with chlorinated ethyl chloride.

4. *Chlorine* and *bromine* convert aldehydes into chlorides of acid radicles:

$$\underset{\text{Aldehyde.}}{C^2H^4O} + Cl^2 = HCl + \underset{\text{Acetyl chloride.}}{C^2H^3O.Cl}$$

$$\underset{\text{Aldehyde}}{C^2H^4O} + 2Cl^2 = 2HCl + \underset{\text{Chloracetyl chloride.}}{C^2H^2ClO.Cl}$$

5. The *alkali-metals* dissolve in aldehydes, eliminating an equivalent quantity of hydrogen:

$$\underset{\text{Aldehyde}}{2C^2H^4O} + K^2 = H^2 + \underset{\text{Potassium aldehyde;}}{2C^2H^3KO}$$

or possibly as follows:

$$6C^2H^4O + K^2 = 3H^2 + 2K(C^2H^3O)^3 \text{ (Wanklyn).}$$

6. Aldehydes treated with *hydrocyanic acid*, *hydrochloric acid*, and *water*, are

converted into an ammonium-salt, or an amidated acid, containing an additional atom of carbon, the former reaction taking place chiefly in the aromatic series, the latter in the fatty series:

$$\underset{\text{Acetic aldehyde.}}{C^2H^4O} + CNH + H^2O = \underset{\text{Amidropropionic acid (alanine).}}{C^3H^7NO^2}$$

$$\underset{\text{Benzoic aldehyde.}}{C^7H^6O} + CNH + 2H^2O = \underset{\text{Ammonium formobenzoate.}}{C^8H^7(NH^4)O^3}$$

7. All aldehydes combine with *aniline*, the reaction taking place between 2 molecules of aniline and 1 or 2 molecules of the aldehyde, with elimination of 1 or 2 molecules of water; thus:

$$\underset{\text{Aniline.}}{2(C^6H^5)H^2N} + \underset{\text{Aldehyde.}}{C^2H^4O} = \underset{\text{Ethylidene-diphenamine.}}{\left.\begin{matrix}(C^2H^4)''\\(C^6H^5)^2\\H^2\end{matrix}\right\}N^2} + H^2O.$$

$$\underset{\text{Aniline.}}{2(C^6H^5)H^2N} + \underset{\text{Aldehyde.}}{2C^2H^4O} = \underset{\text{Diethylidene-diphenamine.}}{\left.\begin{matrix}(C^2H^4)^2\\(C^6H^5)^2\end{matrix}\right\}N^2} + 2H^2O.$$

The resulting compounds are isomeric with the diamines derived from the glycols. This reaction is perfectly general, and may be used, as well as the reaction with alkaline bisulphites, for the recognition of aldehydes (Schiff, *Ann. Ch. Pharm. Suppl.* iii. 343; *Jahresb.* 1864, p. 413).

8. Aldehydes also form crystalline compounds with the *acid sulphites of monamines*; thus valeraldehyde forms with amylamine bisulphite the compound $C^5H^{13}N.SH^2O^3.C^5H^{10}O$; and similar compounds are formed by œnanthol and bitter almond oil. These compounds are soluble in water and in alcohol; they decompose at 100°, water and sulphurous anhydride being given off, and the aldehydes reacting with the bases so as to form diamines like those above mentioned (Schiff, *Zeitschr. f. Chem.* [2] iv. 11).

9. Aldehydes act upon *urea*, either in the solid state or in alcoholic solution, in such a manner as to form condensed ureas containing aldehyde-residues,—compounds which may be represented by the general formula

$$xCH^4N^2O + yC^nH^mO - yH^2O;$$

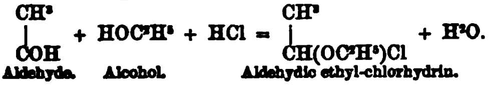
and by further treating these products with aldehydes, ureas of a still higher degree of condensation are obtained. A solution of urea in absolute alcohol forms with *œnanthol* colourless needles of *œnanthyl-diurea*, $(CO)^2N^4H^6(C^7H^{14})''$. By the direct action of œnanthol on solid urea, *diœnanthyl-triurea*, $(CO)^3N^6H^8(C^7H^{14})^2$, is produced; and these compounds heated to 100° with œnanthol are converted respectively into *triœnanthyl-tetra-urea*, $(CO)^4N^8H^{10}(C^7H^{14})^3$, and *pentœnanthyl-hexurea*, $(CO)^6N^{12}H^{14}(C^7H^{14})^5$. Similar compounds are obtained with benzoic aldehyde. All these compounds are resolved by boiling water into aldehydes and urea, and by heating above their melting points, into decomposition-products of urea, and ammonia derivatives of the aldehydes (H. Schiff, *Compt. rend.* lxv. 801; *Jahresb.* 1867, p. 498).

In addition to these general reactions, there are others which are limited to particular classes of aldehydes.

The aldehydes $C^nH^{2n}O$ are resinified by *alcoholic potash*; unite directly with *ammonia*, forming crystalline compounds; are oxidised by *nitric acid*, without formation of substitution-products; and have a great tendency when left to themselves to change into polymeric compounds. Heated with *slaked lime*, they yield the calcium salt of the corresponding acid, together with the corresponding alcohol; e.g.,

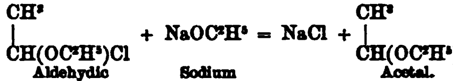
$$\underset{\text{Valeral.}}{4C^5H^{10}O} + \underset{\text{Calcium hydrate.}}{CaH^2O^2} = \underset{\text{Calcium valerate.}}{(C^5H^9O^2)^2Ca} + \underset{\text{Amyl alcohol.}}{2C^5H^{12}O}.$$

When *hydrochloric acid gas* is passed into a solution of one of these aldehydes in absolute *alcohol*, a compound is formed containing the elements of the aldehyde and those of ethylic chloride: e.g.,



$$\underset{\text{Aldehyde.}}{\begin{matrix}CH^3\\|\\COH\end{matrix}} + \underset{\text{Alcohol.}}{HOC^2H^5} + HCl = \underset{\text{Aldehydic ethyl-chlorhydrin.}}{\begin{matrix}CH^3\\|\\CH(OC^2H^5)Cl\end{matrix}} + H^2O.$$

The chlorinated compounds thus formed are isomeric with the glycolic chlorhydrins; thus the ethylic compound formed as above is isomeric with glycolic or ethylenic ethyl-chlorhydrin. $\begin{array}{l}CH^2Cl\\ |\\ CH^2(OC^2H^5)\end{array}$. When treated with ***sodium ethylate***, they exchange their chlorine for oxethyl, OC^2H^5, forming compounds called **acetals**, containing the elements of the aldehyde and ethylic oxide, and isomeric with the glycolic ethers; thus in the acetic series:



$$\begin{array}{l}CH^3\\ |\\ CH(OC^2H^5)Cl\end{array} + NaOC^2H^5 = NaCl + \begin{array}{l}CH^3\\ |\\ CH(OC^2H^5)^2\end{array}$$

Aldehydic ethyl-chlorhydrin. Sodium ethylate Acetal.

Acrolein or acrylic aldehyde, C^3H^4O, the only known aldehyde of the series $C^nH^{2n-2}O$, is similar in most of its reactions to the aldehydes $C^nH^{2n}O$, but when submitted to the action of powerful oxidising agents it yields, not only acrylic acid, $C^3H^4O^2$, but likewise a small quantity of acetic acid, $C^2H^4O^2$.

The aromatic aldehydes, $C^nH^{2n-8}O$, are not resinified by *alcoholic potash*, but acted upon in the same manner as the aldehydes $C^nH^{2n}O$ are acted upon by slaked lime, yielding the corresponding acid and alcohol; e.g.,

$$\underset{\text{Benzoic aldehyde.}}{2C^7H^6O} + KOH = \underset{\text{Potassium benzoate.}}{C^7H^5KO^2} + \underset{\text{Benzyl alcohol.}}{C^7H^8O}.$$

Ammonia does not combine directly with them, but converts them into hydramides, with elimination of water. With fuming *nitric acid* they form nitro-substitution-products, benzoic aldehyde, for example, yielding nitrobenzoic aldehyde, $C^7H^5(NO^2)O$. When left to themselves they do not form polymeric compounds; but benzoic aldehyde, mixed with hydrocyanic acid, is converted under the influence of alcoholic potash into benzoin, $C^{14}H^{12}O^2$.

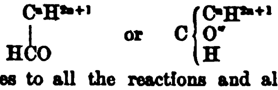
Cinnamic aldehyde, C^9H^8O, the only known member of the series of unsaturated aldehydes, $C^2H^{2n-10}O$, yields by oxidation, benzoic acid, $C^7H^6O^2$, as well as cinnamic acid, $C^9H^8O^2$.

Constitution of Monatomic Aldehydes.—It has been pointed out in the article ALDEHYDES in vol. i. that monatomic aldehydes may be formulated either as hydrides of monatomic oxygenated radicles, or as hydrates of monatomic non-oxygenated radicles, or as oxides of diatomic non-oxygenated radicles: thus for acetic aldehyde we have the three rational formulæ:

$$C^2H^3O.H \qquad \left.\begin{array}{r}C^2H^3\\ H\end{array}\right\}O \qquad (C^2H^4)''.O.$$

The first of these formulæ corresponds to the conversion of aldehydes into acids by oxidation, and by fusion with potash (p. 78); the second, to certain reactions which have been observed only with acetic aldehyde, viz. its conversion into chlorethylidene, C^2H^3Cl, by the action of carbonyl chloride (i. 107), and into vinyl oxide, $(C^2H^3)^2O$, with elimination of water, by the action of certain salts: $2C^2H^3OH - H^2O = (C^2H^3)^2O$. The third formula corresponds to the action of phosphorus pentachloride (p. 78), whereby an aldehyde $C^nH^{2n}O$ is converted into the chloride $C^nH^{2n}Cl^2$; to the action of aniline on aldehydes in general; and to that of ammonia on the aromatic aldehydes.

It is clear that these three formulæ are all included in, and may be deduced from, the constitutional formula

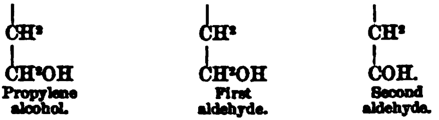


$$\begin{array}{c}C^nH^{2n+1}\\ |\\ HCO\end{array} \quad \text{or} \quad C\left\{\begin{array}{l}C^nH^{2n+1}\\ O''\\ H\end{array}\right.$$

which accordingly applies to all the reactions and all the modes of formation of monotamic aldehydes.

Aldehydes derived from Diatomic Alcohols.

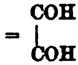
A diatomic alcohol may give rise to two aldehydes, one corresponding to the monobasic, the other to the bibasic acid derived from it. Thus propylene alcohol, $C^3H^8O^2$, might yield the two aldehydes $C^3H^6O^2$ and $C^3H^4O^2$, the first corresponding to lactic, the second to malonic acid:



$$\begin{array}{l}CH^2OH\\ |\\ CH^2\\ |\\ CH^2OH\end{array} \qquad \begin{array}{l}COH\\ |\\ CH^2\\ |\\ CH^2OH\end{array} \qquad \begin{array}{l}COH\\ |\\ CH^2\\ |\\ COH.\end{array}$$

Propylene alcohol. First aldehyde. Second aldehyde.

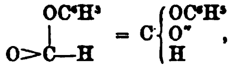
Only a very few of these aldehydes have, however, been obtained.



Of aldehydes derived from the glycols, $C^nH^{2n+2}O^2$, only one is known, namely glyoxal, $C^2H^2O^2 = \begin{array}{l}\text{COH}\\ |\\ \text{COH}\end{array}$, the second aldehyde of ethylene alcohol. This compound has not, however, been actually formed from glycol, but only by oxidation of ethylic alcohol. By a small quantity of nitric acid it is oxidised to glyoxylic acid, $C^2H^4O^4$; by a larger quantity, to oxalic acid, $C^2H^2O^4$. For its other reactions see ii. 920.

Of aldehydes derivable from diatomic alcohols belonging to the other series, and corresponding to monobasic acids, three only are known, viz. salicylol, anisic aldehyde, and furfurol; the relations of these bodies to the corresponding alcohols and acids are shown in the following table:

ALCOHOLS.	ALDEHYDES.	ACIDS.
$C^7H^8O^2$ Saligenin.	$C^7H^6O^2$ Salicylol.	$C^7H^6O^3$ Salicylic acid.
$C^8H^{10}O^2$ Anisic alcohol.	$C^8H^8O^2$ Anisal.	$C^8H^8O^3$ Anisic acid.
$C^5H^6O^2$ Pyromucic alcohol.	$C^5H^4O^2$ Furfurol.	$C^5H^4O^3$. Pyromucic acid.



Salicylol, $C^7H^6O^2 = \begin{array}{l}\quad\text{OC}^6\text{H}^5\\ \quad\ |\\ \text{O}{>}\text{C—H}\end{array} = \text{C}\begin{cases}\text{OC}^6\text{H}^5\\ \text{O}''\\ \text{H}\end{cases}$, is produced by the action of oxidising agents on saligenin, or on salicin, which is a glucoside of saligenin; or on populin, which has the composition of benzoyl-salicin. It is converted by oxidising agents into salicylic acid, and by ammonia into hydro-salicylamide (v. 168). It exhibits the characters of an aldehyde in forming crystalline compounds with alkaline bisulphites, and resembles the phenols in forming saline compounds when acted upon by metallic oxides and hydrates, the metal then taking the place of an atom of hydrogen in the phenyl molecule: thus, sodium salicylol = $C^6H^4NaO.COH$; cupric salicylol = $Cu''(OC^6H^4)^2.(COH)^2$, &c. Sodium salicylol, treated with methyl-iodide, yields **methyl-salicylol**, $C^6H^4(CH^3)O.COH$, a compound exhibiting properties analogous to those of salicylol itself. **Ethyl-salicylol**, $C^6H^4(C^2H^5)O.COH$, is obtained in a similar manner. By treating sodium salicylol with acetic oxide, **aceto-salicylol**, $C^9H^8O^3$, is obtained; thus:

$$\underset{\text{Sodium salicylol.}}{C^6H^4NaO.COH} + \underset{\text{Acetic oxide.}}{(C^2H^3O)^2O} = \underset{\text{Sodium acetate.}}{C^2H^3NaO^2} + \underset{\text{Aceto-salicylol.}}{C^6H^4(C^2H^3O)O.COH}$$

This compound is isomeric with coumaric acid (ii. 93). By peculiar treatment in the process of preparation it may be deprived of a molecule of water, and then yields a *crystalline* substance, $C^9H^6O^2$, identical in every respect with coumarin, the odoriferous principle of the Tonka bean. Further, by treating sodium salicylol with butyric and valeric oxides, butyro-salicylol, $C^6H^4(C^4H^7O)O.COH$, and also valero-salicylol, $C^6H^4(C^5H^9O)O.COH$, are obtained, and these yield by dehydration corresponding homologues of coumarin (Perkin, *Chem. Soc. J.* [2] vi. 53, 181). For details respecting all these compounds see the article SALICYLOL in this volume.

Anisic aldehyde, anisol, or anisyl hydride, $C^8H^8O^2$, is formed, together with anisic acid, by oxidation of anisic alcohol in contact with platinum-black, or, together with oxalic acid, by oxidising anise-oil with warm nitric acid (i. 307). It is converted by oxidation into anisic acid, by ammonia into anishydramide, $C^{24}H^{24}O^3.N^2$, and by alcoholic potash into potassium anisate and anisic alcohol:

$$2C^8H^8O^2 + KOH = C^8H^7KO^3 + C^8H^{10}O^2.$$

Furfurol, $C^5H^4O^2$, the oily liquid produced by distilling bran with dilute sulphuric acid, is shown to be the aldehyde of pyromucic acid by being converted into that acid by oxidation (ii. 752), and into pyromucic acid and the corresponding alcohol by treatment with alcoholic potash (iv. 765):

$$\underset{\text{Furfurol.}}{2C^5H^4O^2} + KOH = \underset{\text{Potassium pyromucate.}}{C^5H^3KO^3} + \underset{\text{Pyromucic alcohol.}}{C^5H^6O^2}$$

There is but one known aldehyde corresponding to a bibasic acid, viz. **phthalic aldehyde**, $C^8H^6O^2 = C^6H^4\begin{cases}\text{CO.H}\\ \text{CO.H}\end{cases}$, derived from phthalic acid, $C^6H^4\begin{cases}\text{CO.OH}\\ \text{CO.OH}\end{cases}$, by substitution of 2 atoms of hydrogen for two equivalents of hydroxyl. It is produced by the action of zinc and hydrochloric acid on phthalic chloride. The aldehyde, extracted from the product by ether and purified by combination with an alkaline bisulphite,

&c., is a white substance having an aromatic odour. It melts at 65°, dissolves easily in alcohol and in ether, sparingly in cold, abundantly in hot water, and crystallises therefrom in small rhombic plates. The warm aqueous solution solidifies with sodium bisulphite to a crystalline mass composed of silky needles (Kolbe a. Wischin, *Chem. Soc. J.* [2] iv. 339).

ALDEHYDINE. NC^8H^{11}.—A base produced by heating a mixture of aldehyde-ammonia, urea, and ammonium acetate to 120°–130°: $4(C^2H^4O.NH^3) = NC^8H^{11} + 3NH^3 + 4H^2O$. It is an oil, boiling at 175°, lighter than water, slightly soluble therein, slightly narcotic, smelling like conine, and containing 4H less than that base; it is *not*, however, converted into conine by treatment with sodium amalgam, and contains 1 mol. H^2O less than Schiff's tetraldine. Aldehydine forms with hydrochloric acid an easily soluble salt, crystallising in needles. Platinic chloride converts it into a resin. With potassium ferricyanide and mercuric nitrate it forms crystalline precipitates (Ador a. Baeyer, *Zeitschr. f. Chem.* [2] iv. 724).

ALIZAREIN. A solution of alizarin in ammonia, which is violet-red when recently prepared, turns blue in about two months at ordinary temperatures, or in 48 hours at 100°, and then yields with hydrochloric acid a violet-coloured precipitate of alizarein or alizaramide, which appears to have the composition $C^{20}H^{12}O^6.NH^3$, or, according to some analyses, $C^{20}H^{12}O^6.3NH^3$ [perhaps $C^{14}H^8O^4.2NH^3$]. It is violet-red while moist, nearly black when dry, unalterable in the air, nearly insoluble in cold water, but soluble in alcohol, forming a reddish-violet solution, from which it is deposited by spontaneous evaporation as a crystalline powder (Schützenberger a. Paraf, *Zeitschr. Ch. Pharm.* 1862, p. 40; Stenhouse, *Proc. Roy. Soc.* xii. 638).

ALIZARIN. Wolff a. Strecker assigned to this body the formula $C^{10}H^6O^3$, founded on certain relations which it was supposed to bear to naphthalene and phthalic acid (i. 113). Schunck, on the other hand, represented it by the formula $C^{14}H^{10}O^4$, founded upon the analyses of alizarin itself, and of its compounds with bases; and finally Graebe a. Liebermann (*Bull. Soc. Chim.* ix. 297) assigned to it the formula $C^{14}H^8O^4$, based upon the conversion of alizarin into anthracene, $C^{14}H^{10}$, by heating with zinc-dust:

$$C^{14}H^8O^4 + Zn^5 + H^2O = C^{14}H^{10} + 5ZnO.$$

The correctness of this formula has lately been strikingly confirmed by the further discovery of Graebe a. Liebermann (*Bull. Soc. Chim.* [2] xi. 516) that alizarin may also be produced from anthracene by the following series of processes, which neither increase nor diminish the number of carbon-atoms in the molecule:

1. Conversion of anthracene into oxanthracene or anthraquinone, $C^{14}H^8O^2$, by oxidation.

2. Conversion of this latter compound by the action of bromine into dibromanthraquinone, $C^{14}H^6Br^2O^2$.

3. Conversion of dibromanthraquinone into alizarin, $C^{14}H^8O^4$, by heating it with an alkali, the change consisting in the replacement of Br^2 by $(OH)^2$. The details of the process will be given further on.

Further confirmation of the formula $C^{14}H^8O^4$ is afforded by some analyses of alizarin (from madder) made by Strecker in 1864 (*Zeitschr. f. Chem.* [2] iv. 263). Schunck's analyses also agree very nearly with the same formula.

According to Rochleder (*Ann. Ch. Pharm.* lxxxii. 205), morindone, the substance obtained by the decomposition of morindin (iii. 1049) by heat, is probably identical with alizarin; and this view is corroborated by Stenhouse (*Chem. Soc. J.* [2] ii. 333), who indeed regards *Morinda citrifolia* as the best source of alizarin, since it yields that substance free from purpurin. W. Stein, on the other hand (*J. pr. Chem.* xcvii. 234), denies the identity of morindone with alizarin, inasmuch as, according to his experiments, morindone gives with sulphuric acid an indigo-blue solution which afterwards turns purple-red, whereas alizarin gives at once a purple-red solution; ferric chloride colours the alcoholic solution of morindone blackish-green, that of alizarin red-brown; and lastly morindone when oxidised by nitric acid yields only phthalic acid, whereas alizarin yields both phthalic and oxalic acids. Stein gives provisionally for morindone the formula $C^{14}H^8O^3$. Respecting Bolley's views of the composition of alizarin and other colouring matters of madder see *Zeitschr. Ch. Pharm.* 1864, p. 174; 1866, p. 112; *Jahresb.* 1864, p. 544; 1866, p. 643).

Alizarin is reduced by *nascent hydrogen*. The violet-coloured solution of alizarin in potash turns brownish-yellow in contact with zinc or iron, and if then supersaturated with an acid, yields a brownish-yellow precipitate richer in hydrogen than alizarin. This substance is easily alterable; when heated it yields a red sublimate of regenerated alizarin, leaving an abundant carbonaceous residue, and is quickly reconverted into alizarin by oxidation in alkaline solution (Bolley, *Jahresb.* 1866, p. 644). According to Schützenberger (*Dictionnaire de Chimie*), alizarin is also easily reduced in alkaline solution by *stannous salts* or by *aldehyde*, the solution changing from blue to orange, and yielding yellow flocks when saturated with an acid.

Alizarin treated with excess of *hydriodic acid* is converted into a mixture of hydrocarbons, chiefly saturated, the most abundant being sextane and octane:

$$C^{14}H^8O^4 + 32HI = C^6H^{14} + C^8H^{18} + 4H^2O + 16I^2$$

(Berthelot, *Bull. Soc. Chim.* [2] ix. 207).

Alizarin treated with fuming *nitric acid* yields a yellow, crystalline, but very unstable, product, which when boiled with water, gives off nitrogen dioxide and yields a deposit of nitroxyalizarin, $C^{14}H^7(NO^2)O^4$. This compound is a red crystalline powder, which dissolves in alcohol and ether, with red colour also in potash, and with light-red colour in boiling alum-solution (Strecker, *Bull. Soc. Chim.* [2] xi. 260).

Preparation of Alizarin. — E. Kopp (*Bull. Soc. Chim.* [2] ii. 231) prepares pure alizarin from his green alizarin (see MADDER, iii. 749) as follows. The green alizarin is boiled for about a quarter of an hour with 15 to 20 times its weight of hydocarbon-oils or paraffins (obtained from any source whatever, purified by distillation over quicklime, boiling not above 150°); and the brownish-yellow oil, which quickly clarifies, is poured off as soon as it has cooled to 100°, and mixed, by repeated and violent agitation, with about ⅛th of its bulk of weak soda-ley (5 to 8 per cent.). The violet-blue alkaline solution is then separated from the oil, and decomposed by dilute sulphuric acid, and the precipitate is purified by washing. Three or four boilings are sufficient for the complete exhaustion of the crude green alizarin. The black residue yields by oxidation with nitric acid a colouring matter called *xanthazarin* (v. 1049).

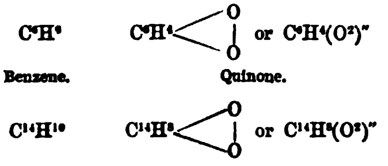
According to J. W. Young (*Chem. News*, xii. 296), small quantities of alizarin may be conveniently prepared by cautiously heating the residue of the alcoholic extract of good garancin in a porcelain dish covered with bibulous paper [pierced with holes?]. The sublimed alizarin collects in a beaker glass inverted over the dish.

A method of preparing alazarin by the transformation of other colouring matters of madder is given by M. Martin of Avignon (*Bull. Soc. Chim.* [2] viii. 463).

According to Bolley (*Jahresb.* 1866, p. 644), purpurin is partially converted into alizarin by the action of a strong heat, in sealed glass tubes, between 210° and 220°.

Separation of Alizarin and Purpurin.—Purpurin dissolves pretty freely in water at 25° to 55°, whereas alizarin begins to dissolve only at 75°. A separation of these principles may therefore be effected by passing a jet of steam into water containing madder in suspension, at such a rate as to keep the temperature constantly at 55°, never allowing it to rise higher, and repeating this treatment till the wash-waters run off quite colourless. On adding lime-water, or, better, baryta-water, to these waters, purpurin is precipitated in the form of a lake, from which it may be separated by hydrochloric acid, and, if necessary, further purified by solution in wood-spirit. The madder thus freed from purpurin is next to be dried and treated several times with wood-spirit, in vessels heated by steam. The resulting solution, poured into cold water slowly and with constant stirring, deposits a hydrate of alizarin, less soluble than alizarin itself. The precipitate after desiccation is almost chemically pure alizarin. Madder thus treated yields from 2 to 3 per cent. of purpurin and 4 to 4½ per cent. of alizarin (Leitenberger, *Bull. Soc. Chim.* [2] x. 333).

Preparation from Anthracene.—The conversion of anthracene into alizarin is made, as already observed (p. 82), by three stages: (1) Anthracene, $C^{14}H^{10}$, is converted into anthraquinone (Anderson's oxanthracene), $C^{14}H^8O^2$, a compound related to anthracene in the same manner as ordinary quinone, $C^6H^4O^2$, to benzene, thus:



C^6H^6 Benzene. $C^6H^4{<}\overset{O}{\underset{O}{|}}$ or $C^6H^4(O^2)''$ Quinone.

$C^{14}H^{10}$ Anthracene. $C^{14}H^8{<}\overset{O}{\underset{O}{|}}$ or $C^{14}H^8(O^2)''$ Anthraquinone.*

This transformation is effected either by heating 1 pt. anthracene with 2 pts. potassium dichromate and sulphuric acid, or by heating 1 pt. anthracene with 2 pts. potassium dichromate and 1 pt. glacial acetic acid. The anthraquinone thus obtained is purified by washing with water and solution in alcohol or benzene, from which it crystallises in yellow needles.

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* Respecting the molecular structure of anthracene and its derivatives, see AROMATIC SERIES.

2. The anthraquinone is either directly converted into dibromanthraquinone by heating it with bromine to 80°–130°:

$$C^{14}H^{8}(O^{2})'' + 2Br^{2} = 2HBr + C^{14}H^{6}Br^{2}(O^{2})'',$$

or 1 mol. anthracene is treated with 8 at. bromine, whereby tetrabromanthracene is formed:

$$C^{14}H^{10} + 4Br^{2} = 4HBr + C^{14}H^{6}Br^{4},$$

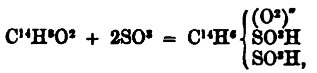
and this last compound is converted into dibromanthraquinone by means of either of the oxidising mixtures above mentioned. In this series of processes, chlorine may be used instead of bromine, but it does not appear to yield equally good results.

3. The transformation of dibromanthraquinone into alizarin is effected by heating it to 130°–260° with caustic potash or soda:

$$C^{14}H^{6}Br^{2}(O^{2})'' + 2KHO = 2KBr + C^{14}H^{6}(OH)^{2}(O^{2})''.$$

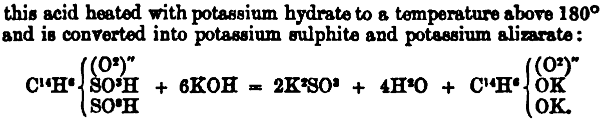
A blue colour is thereby produced, which gradually becomes deeper, the operation being completed when the depth of the tint no longer increases. The saline mass, when cold, is treated with water, the solutions are filtered, and an acid is added in excess, whereby a yellow precipitate is formed, consisting of alizarin. This, after washing with water and drying at a gentle heat, is identical in every respect with alizarin obtained from madder, and yields exactly similar colours when used for dyeing and printing (Graebe a. Liebermann, *Brevet*, No. 83,557; *Bull. Soc. Chim.* [2] xi. 516; *Moniteur scientifique*, No. 296, Avril 15^{me}, 1869; *Zeitschr. f. Chem.* [2] v. 602).

The formation of alizarin in this manner affords the first example of the synthetical product of a natural colouring matter. The process could not, however, be carried out on the manufacturing scale until some reagent had been discovered, less expensive than bromine, which could be used in its stead for effecting the conversion of the anthraquinone. This great improvement has been made by Perkin, who has shown that anthraquinone when strongly heated with sulphuric acid, is converted into *disulph-anthraquinonic* acid:



$$C^{14}H^{8}O^{2} + 2SO^{3} = C^{14}H^{6}\begin{cases}(O^{2})''\\ SO^{3}H\\ SO^{3}H,\end{cases}$$

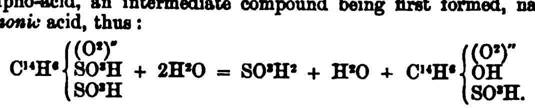
and that this acid heated with potassium hydrate to a temperature above 180°, becomes coloured and is converted into potassium sulphite and potassium alizarate:



$$C^{14}H^{6}\begin{cases}(O^{2})''\\ SO^{3}H\\ SO^{3}H\end{cases} + 6KOH = 2K^{2}SO^{3} + 4H^{2}O + C^{14}H^{6}\begin{cases}(O^{2})''\\ OK\\ OK.\end{cases}$$

The alizarin thrown down from this alkaline product by hydrochloric acid is generally of a bright yellow colour, and quite as pure as the analogous precipitate obtained when dibromanthraquinone is used.

The formation of alizarin, however, is not the primary result of the action of potash on the disulpho-acid, an intermediate compound being first formed, namely, *sulph-oxanthraquinonic* acid, thus:



$$C^{14}H^{6}\begin{cases}(O^{2})''\\ SO^{3}H\\ SO^{3}H\end{cases} + 2H^{2}O = SO^{3}H^{2} + H^{2}O + C^{14}H^{6}\begin{cases}(O^{2})''\\ OH\\ SO^{3}H.\end{cases}$$

This acid is crystalline and of a yellow or orange colour, easily soluble in water, and yields blue or violet solutions with alkalis. When heated with potash it decomposes, yielding sulphurous acid and alizarin (Perkin, *Chem. Soc. J.* [2] viii. 133).

ALKALIS. According to Debray (*Bull. Soc. Chim.* [2] v. 404), *phosphomolybdic acid* affords a delicate test for certain alkali-metals, as well as for ammonia and organic bases. Potassium, cæsium, rubidium, and thallium are precipitated by it from acid solutions; sodium, lithium, and other metals give no precipitates. This test will indicate the presence of 1 pt. of potassium hydrate in 500 pts. of liquid. All the precipitates are yellow, very slightly soluble, and contain only very small quantities of the alkali-metal. The phosphomolybdic acid used for this reaction is prepared by boiling the yellow ammonium phosphomolybdate with nitromuriatic acid.

Böttger (*J. pr. Chem.* ci. 290) recommends the alcoholic extract of the leaves of *Coleus Verschaffelti* as a delicate test for alkalis. To prepare it, the fresh leaves are agitated with absolute alcohol acidulated with a few drops of sulphuric acid, and the digestion is continued for twenty-four hours. The tincture imparts to paper a fine red colour, which is turned green by alkalis. Paper thus prepared is very sensitive; a strip of it held before a jet of coal gas is soon turned green by the ammonia in the gas.

A solution of *sodium nitroprusside* yields the well-known purple coloration with soluble metallic sulphides, but not with hydrogen sulphide. Hence a solution of this salt mixed with hydrogen sulphide affords an extremely delicate test of the alkalinity of a solution, such a mixture turning blue in contact, not only with free alkalis, but likewise with alkaline carbonates, bicarbonates, borates, silicates, phosphates, and, in short, with all salts of the alkali-metals which turn litmus-paper blue (Filhol, *Zeitschr. f. Chem.* [2] iv. 568).

Stolba (*ibid.* 94) recommends a solution of cupric silicofluoride as a precipitant for alkalis; it keeps well and does not corrode glass vessels.

ALKALOÏDS. Compounds of alkaloïds, natural and artificial, with *iodine monochloride* have been prepared by W. A. Tilden (*Chem. Soc. J.* [2] iv. 145). They are obtained by mixing the aqueous solution of iodine monochloride with the acidulated hydrochloride of the base. A precipitate is formed which soon becomes crystalline, and in some cases may be recrystallised without decomposition from hydrochloric acid. With *tetrethylammonium chloride*, fern-like crystals are formed containing $(C^2H^5)^4NCl^2I$ (v. 731); with *triethylammonium chloride*, the compound $(C^2H^5)^3HNCl^2I$, which crystallises in slender, easily decomposible needles. The *caffeine compound* $C^8H^{10}N^4O^2.HCl.ICl$ forms crystals, apparently having the form of oblique rhombic prisms. The precipitate formed with *quinine hydrochloride* is yellow, and becomes darker in colour when recrystallised from dilute hydrochloric acid.

Periodides of several alkaloïds have been obtained by Jörgensen (*Zeitschr. f. Chem.* [2] v. 673). (See the several ALKALOÏDS.)

According to R. Palm (*Jahresb.* 1863, p. 433), many alkaloïds combine with *sulphur* in one or more proportions. Some, as morphine, atropine, papaverine, form only monosulphides; others, as quinine, strychnine, codeine, thebaine, berberine, veratrine, delphinine, and aconitine, form monosulphides and polysulphides; and a few, as trimethylamine and conine, form monosulphides, polysulphides, and sulphydrates. Some of the weaker bases, as cinchonine, brucine, narcotine, and emetine, do not combine with sulphydric acid. The sulphides corresponding to the metallic monosulphides are produced by mixing a salt of the alkaloïd with a soluble metallic sulphide, or by precipitating the alcoholic solution of the base with hydrogen sulphide; the polysulphides, by precipitation with a metallic polysulphide (such as K^2S^3); the sulphydrates of trimethylamine and conine, by saturating the base with sulphydric acid. The sulphur-compounds of the oxygenated bases are amorphous or crystalline, colourless, yellow, or red-brown precipitates, which, with a few exceptions, are decomposed by drying, or even by keeping.

Detection and Separation of Alkaloïds. — According to J. Trapp (*Jahresb.* 1863, p. 702), the yellow pulverulent or flocculent precipitates produced in the acid solutions of many organic bases by *phosphomolybdic acid* are insoluble in dilute nitric acid, but easily soluble in ammonia and the fixed alkalis. The solutions of the several precipitates in ammonia exhibit the following colour-reactions:

	Precipitate.	Solution in Ammonia.	On boiling.
Aconitine Atropine Bebeerine Berberine	yellow	blue	colourless.
Brucine	orange	yellow-green	brown.
Codeine	yellow	green	orange-red.
Quinine Quinidine	yellow	insoluble	colourless.
Caffeine	yellow	colourless	—
Conine	yellowish-white	light-blue	colourless.

With digitaline ($\frac{1}{100}$ of a grain) and phosphomolybdic acid there is formed a yellow liquid, which becomes green on boiling, deep indigo-blue on addition of ammonia, green again on heating, and then colourless.

Metatungstic acid (v. 911) is, according to Scheibler (*Jahresb.* 1860, p. 157), a more delicate reagent for alkaloïds than phospholybdic acid, all such bases being precipitated by it in white flocks. To obtain this reaction it is not necessary to use pure metatungstic acid, as it is produced equally well by a solution of a metatungstate mixed with any mineral acid, or even by ordinary sodium tungstate mixed with phosphoric acid—the so-called *phosphotungstic acid*—inasmuch as phosphoric acid removes part of the base from an ordinary tungstate and converts it into a metatungstate. Some alkaloïds, as morphine, narcotine, and nicotine, are also precipitated by the so-called *phosphantimonic acid*, prepared by dropping antimonic chloride into aqueous phosphoric acid (F. Schulze, *Ann. Ch. Pharm.* cix. 179).

Potassio-mercuric iodide, first recommended by De Vrij (*Jahresb.* 1867, p. 602) as a very delicate test for strychnine, likewise produces in solutions of nearly all non-volatile alkaloïds, yellowish-white precipitates insoluble in acids and in dilute alkalis, slightly soluble in excess of the reagent, easily soluble in alcohol, and generally also in ether. Strychnine is precipitated from solutions containing only 1 pt. of the base in 100,000; with volatile bases the reaction is not delicate. Theobromine and caffeine, bitter principles, carbohydrates, and organic acids are not precipitated by potassio-mercuric iodide; but with albuminous and gelatinous substances, and with extractive matters, in presence of free acid (but not in alkaline solutions) it forms tenacious elastic precipitates (A. Valser, *Zeitschr. anal. Chem.* ii. 79). According to F. J. Mayer (*Ann. Ch. Pharm.* cxxxiii. 236), the precipitation of alkaloïds from acid solutions may be effected as completely by potassio-mercuric iodide (in some cases also by mercuric bromide or cyanide) as by phosphomolybdic or phosphotungstic acid. It is best to apply this reagent to the solution obtained by treating either the vegetable substance itself or its aqueous extract with acidulated alcohol. The precipitates vary greatly in composition. They are, with a few exceptions (as with morphine), sparingly soluble in water, pulverulent, or (as with the volatile bases) resinous and gummy. To separate the base, the precipitate is triturated with stannous chloride and a sufficient quantity of potash-ley to render the mass strongly alkaline, and the basic is then extracted with ether or chloroform, or, if insoluble therein, with strong alcohol, after addition of pulverised sodium carbonate.

According to Dragendorff (*Zeitschr. anal. Chem.* v. 405), *potassio-bismuthous iodide* (prepared by treating sublimed bismuth iodide with a hot concentrated solution of potassium iodide, and mixing the decanted liquid with an equal volume of the same solution) may also be used for the precipitation of organic alkaloïds. Its solution, slightly acidulated with sulphuric acid and added to the very dilute solutions of most vegetable alkaloïds (likewise acidulated with sulphuric acid), forms almost instantly a flocculent precipitate having the colour of precipitated antimonious sulphide. The double chlorides of iridium and rhodium also give precipitates with some bases (strychnine and brucine).

A volumetric process for estimating morphine and other alkaloïds by means of potassio-mercuric iodide has been given by F. F. Mayer (see MORPHINE, iii. 1053).

The following alkaloïds are precipitated by *potassio-cadmic iodide*, even from very dilute solution, acidulated with sulphuric acid: nicotine, conine, piperine, morphine, codeine, thebaine, narcotine, quinine, quinidine, cinchonine, strychnine, brucine, veratrine, berberine, atropine, hyoscyamine, aconitine, delphinine, emetine, curarine, and cytisine. The precipitates are white and flocculent at first, but mostly become crystalline. Quinine and strychnine are entirely precipitated, even when diluted with 10,000 pts. of water. These precipitates are insoluble in ether, soluble in alcohol, slightly soluble in water, soluble in excess of potassio-cadmic iodide. They give up their alkaloïd when agitated with a suitable solvent, after addition of an alkali. They are closely analogous to the compounds of the alkaloïds with the iodomercurides and iodobismuthides (Marmé, *Bull. Soc. Chim.* [2] ix. 203).

Respecting the precipitation of alkaloïds by *sodium nitroprusside*, see Horsley (*Chem. News*, v. 355).

Many alkaloïds and salts of alkaloïds, when heated with an alkaline solution of *potassium permanganate*, give off half their nitrogen in the form of ammonia; such is the case with morphine, codeine, papaverine, strychnine, methylstrychnine-iodide, brucine, the sulphates of quinine and cinchonine, nicotine, naphthylamine, toluidine, and acetate of rosaniline. Creatine similarly treated gives off a third of its nitrogen as ammonia; theine, a fourth (Wanklyn and Chapman, *Chem. Soc. J.* [2] viii. 161).

Dragendorff recommends the use of *benzene* as a solvent for separating alkaloïds from substances with which they may be mixed, as in toxicological investigations. The crude aqueous extract of the substance under examination is first freed from foreign substances by means of benzene, and after neutralisation more benzene is added to dissolve out the base. The separation of the benzene as a distinct layer is facilitated by heating the liquid to 50° or 60°, or by addition of a little alcohol. This mode of separation is applicable to strychnine, veratrine, atropine, aconitine, quinine, cinchonine, quinidine, codeine, narcotine, thebaine, papaverine, conine, and nicotine (for the last two, however, and for atropine, on account of their volatility, ether is to be preferred to benzene). Caffeine, theobromine, colchicine, piperine, curarine, narceine, and berberine cannot be separated in this way, because they are already dissolved out by benzene from the acid solution; neither can the method be applied to morphine or solanine, which are nearly insoluble in benzene.

β. To detect the presence of alkaloïds in organic liquids, strychnine in beer for example, R. Wagner (*Zeitschr. anal. Chem.* iv. 387) mixes the liquid, diluted with 2 vol. water (½ to one litre), with about 5 c. c. of a solution of iodine in potassium iodide (12·7 grms. iodine to the litre), and a few drops of sulphuric acid; dissolves the precipitate, separated from the supernatant liquid, in a dilute solution of sodium hyposulphite, and separates it again by means of the iodine solution. If this new precipitate be now dissolved in aqueous sulphurous acid, the solution will leave on evaporation the pure sulphate of the base.

According to Grandeau (*Bull. Soc. Chim.* [2] ii. 74), alkaloïds, such as morphine, brucine, and digitaline, contained in solutions, together with animal substances, (urine, &c.), may be easily separated from the latter by dialysis, and obtained in the pure state by treating the evaporated residue of the dialysate with alcohol. According to A. T. Machattie (*Chem. News*, x. 183), strychnine, as well as arsenious acid, may be separated by dialysis, if, instead of parchment paper, the membranes of the stomach or intestines be employed as the diaphragm.

Helvig has shown (*Zeitschr. anal. Chem.* iii. 43; *Jahresb.* 1864, 726) that many organic bases may be obtained in a state fit for microscopic examination by *sublimation*. A very small quantity of the finely pulverised base is cautiously heated on a piece of platinum foil, having a hemispherical depression in the middle, and covered at that part with a small glass plate such as are used for mounting microscopic objects: the sublimate then collects on the glass, and may be easily examined with a magnifying power of 80. Morphine thus treated yields a layer of round granules, which in contact with a drop of water, and somewhat more slowly with ammonia, are converted into six-sided prisms; with dilute hydrochloric acid, into tufts of long needles. Dilute chromic acid, on the contrary, does not give rise to any formation of crystals. The sublimate exhibits the reaction of morphine with iodic acid and starch, that is to say, it reduces the iodic acid, and consequently turns the starch blue. *Strychnine* yields a similar amorphous sublimate, which when moistened with water changes into four-sided prisms laid over one another in stars or crosses, with ammonia into quadratic octohedrons, or characteristic short, truncated, four-sided prisms. Hydrochloric acid forms, sometimes tufts of needles, sometimes broad four-sided prisms; dilute chromic acid forms the yellow stellate crystals and double pyramids of strychnine chromate; and strong sulphuric acid with potassium bichromate produces the well-known colorisation. *Brucine* yields a similar granular sublimate, which, however, seldom becomes crystalline with water or with hydrochloric acid, more easily with sulphuric or nitric acid, and is converted by ammonia into a deep yellow amorphous mass; with chromic acid, it gradually forms dark yellow stars or rosettes composed of short prisms. *Veratrine* sublimes in crystals, partly having the form of a rather long distorted rectangle, partly of stars composed of needles or four-sided laminæ. *Aconitine* forms an amorphous sublimate, which in contact with ammonia produces characteristic crystalline formations like the tin-tree (needles arranged in cruciform groups). *Atropine* sublimes very easily in transparent drops, which in contact with hydrochloric acid change in the course of 24 hours into distinct octohedrons. *Solanine* sublimes as a network of tuft-like or lozenge-shaped groups of slender needles. *Digitaline* does not yield a characteristic sublimate.

On the microscopic characters of organic alkaloïds, see also Helvig's *Das Mikroscop in der Toxicologie*, Mainz, 1864; Deane and Brady, *On Microscopic Research in Relation to Pharmacy* (*Chem. Soc. J.* [2] iii. 34); Wormly, *The Micro-chemistry of Poisons*, New York, 1867; Erhard (*N. Jahrb. Pharm.* xxv. 129, 193, 283; xxvi. 9, 129).

Alkaloïds of Opium.—Kubly (*Jahresb.* 1866, p. 823) has determined the solubility of the several opium alkaloïds in benzene and in amyl alcohol. The results obtained at ordinary temperatures are given in the following table:

100 pts. amyl alcohol dissolve:		100 pts. benzene dissolve:	
Morphine	0·260	Morphine	0
Narcotine	0·325	Narcotine	4·614
Papaverine	1·30	Papaverine	3·73
Thebaine	1·67	Thebaine	5·27
Codeine	15·68	Codeine	9·60

If the solution of these bases obtained by extraction with acids be supersaturated with alkali, and repeatedly treated while warm with benzene, *narcotine*, *papaverine*, *thebaine*, and *codeine* will pass into solution; and the aqueous liquid will then give up to hot amyl alcohol the *morphine*, and after evaporation to dryness it will yield to hot ethyl alcohol the *narceine*. For the approximate separation of the four bases first named Kubly treats the residue left on evaporation of the benzene with a small quantity of cold amyl alcohol, which dissolves chiefly the *codeine*; he then digests the residue with water containing acetic acid, to dissolve out the *papaverine* and *thebaine*, the *narcotine* remaining undissolved. *Papaverine* and *thebaine* may be separated in sulphuric acid solution by potassio-bismuthous iodide, which dissolves only the *thebaine*. The use of ethyl acetate (100 pts. of which dissolve 0·213 pts. morphine), instead of amyl alcohol, for extracting the morphine, is, according to Kubly, attended with considerable loss of the alkaloïd.

Dragendorff (*Jahresb.* 1864, p. 727) has examined the reactions of the opium alkaloïds with sulphuric acid, both pure and containing nitric acid. *Codeine* dissolves slowly in pure sulphuric acid, forming a greenish, or after a week an indigo-blue liquid, which becomes dark-brown at 150°, and after cooling with nitric acid nearly blood-red. With sulphuric acid containing nitric acid the same changes of colour take place, but more quickly. *Papaverine* is coloured dark bluish-violet, both by pure sulphuric acid and by that which contains nitric acid, and dissolves to a reddish-violet liquid, which does not alter at 150°. *Narceine* forms a blood-red liquid, becoming dark-brown to garnet-coloured at 150°, and light red-brown after cooling with nitric acid. Thebaine forms a dark-red to orange-coloured solution, gradually turning to olive-green at 150°. *Porphyroxine* dissolves to a black-brown liquid becoming dark garnet-coloured at 150°. *Chelidonine* is coloured green by sulphuric acid containing nitric acid, at 150° olive-green, and after cooling with nitric acid dark-brown. When *morphine* is boiled with a not too dilute solution of phosphorous or hypophosphorous acid, and the liquid is then mixed with a large quantity of strong sulphuric acid, it assumes a reddish-violet colour, becoming yellowish with a little nitric acid; and if it be then warmed in contact with metallic copper, it gradually assumes a greenish and then a splendid blue colour. *Narceine* boiled with hypophosphorous acid, and then poured into strong sulphuric acid, forms a dark cherry-red solution, becoming yellow with nitric acid, and gradually colourless in contact with copper.

Matthiessen a. Wright (*Proc. Roy. Soc.* xvii. 455, 460) have shown that morphine and codeine heated in sealed tubes with hydrochloric acid of ordinary strength are converted, by loss of the elements of water, into apomorphine, $C^{17}H^{17}NO^2$ (*q.v.*).

Alkaloïd produced by Alcoholic Fermentation.—According to J. Oser (*J. pr. Chem.* ciii. 192), the fermentation of sugar by purified yeast is attended with the formation of an alkaloïd containing $C^{13}H^{20}N^4$. Its hydrochloride dried in a vacuum forms a white very hygroscopic laminated mass, which quickly turns brown on exposure to the air, and has a burning taste with very bitter after-taste. This alkaloïd appears to be formed from the azotised constituents of the yeast, and should be found in liquids produced by alcoholic fermentation, such as wine and beer.

ALLANTOÏN. $C^4H^6N^4O^3$.—This substance is converted by hydriodic acid into hydantoïn (iii. 177) and urea (Baeyer, *Ann. Ch. Pharm.* cxviii. 178), and by water and sodium amalgam into glycoluril, $C^4H^6N^4O^2$ (v. 960) (Strecker a. Rheineck, *ibid.* cxxxi. 119):

$$\underset{\text{Allantoïn.}}{C^4H^6N^4O^3} + H^2 = \underset{\text{Glycoluril.}}{C^4H^6N^4O^2} + H^2O.$$

$$\underset{\text{Allantoïn.}}{C^4H^6N^4O^3} + 2HI = \underset{\text{Hydantoïn.}}{C^3H^4N^2O^2} + \underset{\text{Urea.}}{CH^4N^2O} + I^2.$$

ALLOCLASE. A mineral from Orowicza, in the Bannat, formerly regarded as a radial cobalt-glance. It occurs generally in steel-grey, broadly cauliform aggregates, more rarely in separate crystals belonging to the rhombic system, and exhibiting the combination $\infty P\ .\ \breve{P}\infty$. Angle $\infty P : \infty P = 106°$; $\breve{P}\infty : \breve{P}\infty = 58°$. Cleavage perfect, both prismatic and basal. Hardness above 4. Sp. gr. = 6·6. According to an analysis by Heine, it contains:

S	As	Bi	Au	Fe	Zn	Co	Ni	
16·22	32·69	30·15	0·68	5·58	2·41	10·17	1.55	= 99·45.

These numbers may be represented by the formula $Co^6As^{10}S^9$, or perhaps $3CoS.3CoAs^2 . 2As^2S^3$, one-fourth of the arsenic being replaced by bismuth (Tschermak, *Wien. Akad. Ber.* liii. [1] 1; *Jahresb.* 1866, p. 918).

ALLOPHANIC ETHERS. *Ethyl allophanate* is produced, together with oxamide and alcohol, by heating urea with ethyl oxalate in a sealed tube to 135°–170° (Grabowski, *Ann. Ch. Pharm.* cxxxiv. 115):

$$\underset{\text{Urea.}}{2CH^4N^2O} + \underset{\text{Ethyl oxalate.}}{(C^2H^5)^2C^2O^4} = \underset{\text{Ethyl allophanate.}}{C^2H^5.C^2H^3N^2O^3} + \underset{\text{Alcohol.}}{(C^2H^5)HO} + \underset{\text{Oxamide.}}{C^2H^4N^2O^2}$$

Also, together with hydrochloric acid, by heating equivalent quantities of urea and ethyl chlorocarbonate (i. 916) in a flask provided with an ascending condenser:

$$CH^4N^2O + C^3H^5ClO^2 = HCl + C^2H^5.C^2H^3N^2O^3$$

(Wilm a. Wischin, *Zeitschr. f. Chem.* [2] iv. 5).

Phenyl Allophanate, $C^6H^5.C^2H^3N^2O^3$, is formed by passing cyanic acid vapour into perfectly anhydrous phenol. When dissolved out of the resulting pasty mass with alcohol, and precipitated by ether, it forms slender, inodorous, and tasteless crystals, unctuous to the touch, insoluble in cold water. At 150° it is resolved into phenol and cyanic acid. With alcoholic potash it forms potassium allophanate; with baryta-water, barium allophanate (Tuttle, *Jahresb.* 1857, p. 451).

Oxethyl-acetyl-allophanic Acid. $C^6H^{10}N^2O^5 = C^2H^2(C^2H^5O)(C^2H^3O)N^2O^3$ (also called *oxethyl-glycolyl-allophanic acid*).—An acid formed by heating potassium cyanate with ethyl monochloracetate:

$$\underset{\text{Ethyl chloracetate.}}{C^2H^5.C^2H^2ClO^2} + \underset{\text{Potassium cyanate.}}{2KCNO} + H^2O = KCl + \underset{\text{Potassium oxethyl-acetyl-allophanate.}}{KC^6H^9N^2O^5}$$

When 100 grams of each of these substances are boiled for 15 hours with about 10 vol. of 90 per cent. alcohol, potassium chloride is separated; and the liquid, decanted while still hot and mixed with the alcohol used for washing the potassium chloride, separates, after distillation to $\frac{1}{10}$ of its volume, and admixture with ether, into a supernatant liquid and a semi-crystalline deposit. The liquid yields by spontaneous evaporation ethyl allophanate, formed by the action of alcohol and water on the potassium cyanate:

$$2KCNO + C^2H^6O + 2H^2O = 2KHO + C^2H^5.C^2H^3N^2O^3.$$

The lower layer, when treated with cold water, also yields a small quantity of ethyl allophanate, and the liquid decanted therefrom and mixed with dilute sulphuric acid, deposits after a while crystals of oxethyl-acetyl-allophanic acid. This acid separated from its lead-salt, crystallises in oblique rhombic tables, sparingly soluble in cold water, alcohol, and ether. Its potassium and sodium salts are very soluble and crystallisable; the barium salt, $Ba(C^6H^9N^2O^5)^2$, crystallises in microscopic rhombic tables; the lead-salt, $Pb(C^6H^9N^2O^5)^2$, in sparingly soluble needles; the silver salt is very soluble in water and decomposes when its solution is warmed.

Oxethyl-acetyl-allophanic acid is decomposed by heat, giving off cyanic acid. Boiled with strong potash-ley, it is resolved into glycollic acid, carbonic acid, alcohol, and ammonia:

$$C^6H^{10}N^2O^5 + 5KHO = KC^2H^3O^3 + 2K^2CO^3 + C^2H^6O + 2NH^3.$$

It is not decomposed by nitric or nitrous acid. With strong sulphuric acid it turns brown and gives off a large quantity of carbon dioxide. By boiling with dilute sulphuric acid, it is converted into a new acid (likewise produced in the reaction of ethyl chloracetate on potassium cyanate), which neither crystallises nor forms crystalline salts. This acid is insoluble in ether, and is also converted into glycollic acid by boiling with potash (Saytzeff, *Ann. Ch. Pharm.* cxxxiii. 329).

ALLOXAN and **ALLOXANTIN.** The following method of preparing alloxan from crude uric acid, such as is extracted from guano, is given by Liebig (*Ann. Ch. Pharm.* cxlvii. 366; *Bull. Soc. Chim.* [2] xi. 152). The crude uric acid is added by small portions to nitric acid of sp. gr. 1·42, mixed with 8 to 10 parts of water and heated to 60° to 70°, whereupon abundant frothing takes place, accompanied by the emission of nitrous vapours. When the nitric acid no longer takes up the uric acid, and acquires the colour of onion-peel, the liquid is to be boiled and filtered. On adding to this liquor, which contains alloxan, a concentrated solution of tin in hydrochloric acid mixed with its own volume of that acid, a pulverulent precipitate is formed consisting of alloxantin, which is to be collected, washed, and dried. To reconvert this alloxantin into alloxan, it is moistened with a mixture of 2 parts fuming nitric acid (sp. gr. 1·52) and 1 part ordinary nitric acid (sp. gr. 1·42), whereupon large quantities of nitrous acid are evolved. The reaction is complete in a few days, the mass being then completely soluble in water. This mass is to be drained on a porous tile, dried over the water-bath till all the nitric acid is driven off; and the alloxan is finally crystallised from water. This process yields nearly the theoretical quantity of alloxan.

Alloxan is formed, together with urea, by bringing *bromine* in contract with uric acid suspended in water:

$$\underset{\text{Uric acid.}}{C^5H^4N^4O^3} + Br^2 + 2H^2O = \underset{\text{Alloxan.}}{C^4H^2N^2O^4} + \underset{\text{Urea.}}{CH^4N^2O} + 2HBr.$$

If the mixture be heated during the reaction, parabanic acid, oxalic acid, and ammonium bromide are also formed. *Chlorine* and *iodine* act upon uric acid in the same manner (L. Hardy, *Bull. Soc. Chim.* [2] i. 445).

Anhydrous alloxan heated to 260° is converted into an isomeric modification which is soft and red, and when treated with bases forms salts, called by Hardy isoalloxanates, which are isomeric with the alloxanates (i. 138). The ammonium and silver salts are red precipitates; the ammonio-argentic salt, $C^4H^2(NH^4)AgN^2O^5$, is a blue precipitate. The potassium, sodium, barium, strontium, calcium, lead, and mercury salts also form coloured precipitates (Hardy, *loc. cit.*).

Alloxan or alloxantin boiled for a long time with very dilute sulphuric acid yields a large quantity of ammonium hydurilate (iii. 220); with strong sulphuric acid, there is formed (together with dialuric acid) a sparingly soluble ammonium salt, which differs from the hydurilate in not producing a green colour with ferric salts. When a solution of alloxantin in 3 or 4 parts of strong sulphuric acid is heated as long as sulphurous oxide is evolved, and the resulting yellow solution is mixed with an equal volume of water, a sparingly soluble powder (amounting to 60 per cent. of the alloxantin) is separated, which is resolved by boiling with water into barbituric and parabanic acids. In one experiment, however, hydurilic acid was obtained instead of barbituric acid (Finck, *Ann. Ch. Pharm.* cxxxii. 298).

Bromalloxan or *Dibromo-barbituric acid*, $C^4H^2Br^2N^2O^3$, is described among the derivatives of uric acid (v. 961).

ALLYL. C^6H^{10}.—See DIALLYL (p. 92).

ALLYL ALCOHOL. $C^3H^6O = C^3H^5.OH$.—Produced, together with isopropyl alcohol and acropinacone (p. 56), when acrolein is treated with zinc and hydrochloric acid: $C^3H^4O + H^2 = C^3H^6O$ (Linnemann, *Ann. Ch. Pharm. Suppl.* iii. 257). According to Tollens a. Henninger (*Bull. Soc. Chim.* [2] xi. 394), the best mode of preparing this alcohol is to distil a mixture of glycerin and oxalic acid in certain proportions. Oxalic acid heated with glycerin is resolved, as is well known, into carbon dioxide and formic acid, which latter may be obtained by distilling the mixture with water (ii. 686), or, according to Lorin (*Jahresb.* 1865, p. 296), with a fresh quantity of oxalic acid. But if the mixture be continuously heated without addition either of water or of oxalic acid, the formic acid retained by the glycerin reduces it, and forms allyl alcohol,* which passes into the receiver:

$$\underset{\text{Glycerin.}}{C^3H^8O^3} + \underset{\text{Formic acid.}}{CH^2O^2} = \underset{\text{Allyl alcohol.}}{C^3H^6O} + 2H^2O + CO^2$$

Part of the alcohol is however converted into allyl formate.

Four parts of glycerin are heated with one part of crystallised oxalic acid in a retort provided with a thermometer, the receiver being changed when the temperature rises to 190°, and the distillation continued from that point to 260°. The distillate consists of aqueous allyl alcohol mixed with allyl formate, acrolein, glycerin mechanically carried over, and formic acid. The residue, which consists of glycerin, may be used for a fresh preparation of allyl alcohol by distillation with another portion of oxalic acid. To separate the allyl alcohol, the crude distillate is rectified; and the new distillate is dried over potassium carbonate, freed from allyl formate and acrolein by means of solid potash, again distilled, and freed from the last traces of water by rectification over anhydrous baryta. A quantity of allyl alcohol is thus obtained equal to one-fifth of the weight of the oxalic acid used.

The presence of an alkali in the oxalic acid, uncombined with a stronger acid, greatly interferes with the production of allyl alcohol: hence it is advisable to add from $\frac{1}{2}$ to

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* The reaction really takes place by two stages, monoformin, $(C^3H^5)''$, $(OH)^2(OCOH)$ being first produced by the mutual action of the formic acid and glycerin, and then decomposed, as shown by the equation.

$$(C^3H^5)(OH)^2(CO^2H) = C^3H^5(OH) + H^2O + CO^2.$$

The monoformin may be isolated by heating the mixture of glycerin and oxalic acid to 100° and agitating it with ether.

4 per. cent. of hydrochloric acid or sal-ammoniac to the oxalic acid. The quantity of allyl alcohol produced is in direct proportion to the carbon dioxide evolved above 200°. Free sulphuric acid or a large quantity of hydrochloric acid should be avoided: the latter gives rise to the formation of mono-allylin, $C^3H^5(OH)^2(OC^3H^5)$ (Tollens, *loc. cit.*). According to Swartz (*Zeitschr. f. Chem.* [2] iv. 259), allyl alcohol is formed by heating dichlorhydrin, $C^3H^6Cl^2O$, with solution of potassium iodide:

$$C^3H^6Cl^2O + 2KI = C^3H^6O + 2KCl + I^2.$$

Allyl alcohol boils at 91° (at 103° according to Hofmann a. Cahours), and solidifies at $-$ 54°. It is not completely dehydrated by potassium carbonate (Tollens a. Henninger). It is an unsaturated compound, capable of uniting with 2 atoms of bromine, chlorine, &c., and is not converted into propylic or isopropylic alcohol by the action of nascent hydrogen (Tollens, *ibid.* vi. 268). Its aqueous solution takes up 2 atoms of *bromine*, forming allyl-alcohol bromide, $C^3H^6OBr^2$, isomeric, or perhaps identical, with dibromhydrin. This bromide is a colourless oil, which boils at 219°, and, like dibromhydrin, is resolved by aqueous potash into potassium bromide and glycerin. By *nascent hydrogen*, evolved either by sodium amalgam or by zinc and dilute sulphuric acid, it is converted into a liquid, which appears to be identical with the original alcohol. On mixing it with *zinc-ethyl* in ethereal solution, a large quantity of combustible gas is evolved, and a white solid mass is formed, which when treated with water gives off gas, and is resolved into zinc-oxide and the original bromine-compound (Morkownikoff, *Jahresb.* 1864, p. 490). Allyl alcohol also unites with *chlorine*, forming several products, one of which, boiling at 180°–184°, has the composition of dichlorhydrin, $C^3H^6OCl^2$ (Tollens a. Henninger), and is reconverted into allyl alcohol by nascent hydrogen, like the bromide. Allyl alcohol also unites with iodine, forming a heavy, colourless liquid (Tollens).

ALLYL BROMIDES. The monobromide C^3H^5I, prepared by the action of phosphorus pentabromide on allyl alcohol, is a colourless liquid having an irritating odour; sp. gr. 1·4507 at 0°, 1·438 at 15°; boiling at 70° under a pressure of 753 mm. The isomeric compound bromopropylene boils at 62° according to Reynolds, at 54° according to Vogt. Allyl bromide is decomposed by potassium and silver salts; heated with potassium sulphide, it forms allyl sulphide, boiling at 140°. With alkaline sulphocyanates it yields allyl sulphocyanate, having the properties of volatile mustard-oil (Tollens, *Bull. Soc. Chim.* [2] xi. 397).

Allyl dibromide, $C^3H^4I^2$, and the corresponding *iodide* (i. 141, 142), are, properly speaking, diallyl compounds, $C^6H^{10}Br$ and $C^6H^{10}I^4$ (see DIALLYL).

The *tribromide*, $C^3H^5Br^3$, is converted by prolonged boiling with alcoholic potash into propargyl-ethylic ether, $(C^3H^3)C^2H^5O$ (*q.v.*) (Liebermann, *Ann. Ch. Pharm.* cxxxi. 123; cxxxv. 266).

ALLYL CHLORIDES. The *monochloride*, C^3H^5Cl, was obtained by Hofmann a. Cahours in the same manner as the monobromide (i. 142). Oppenheim (*Ann. Ch. Pharm.* cxl. 204) obtains it by heating allyl oxalate to 100° with an alcoholic solution of calcium chloride; calcium oxalate is then precipitated, and the liquid, mixed with water and distilled in the water-bath, yields allyl chloride. An easier mode of preparation is to mix allyl iodide with an equal volume of alcohol, and then with a slight excess of mercuric chloride. Mercuric iodide is then formed, with great evolution of heat, and on adding water to the distillate, a liquid separates containing allyl chloride in the portion boiling between 43° and 50°, and probably allyl-ethylic oxide in the portion of higher boiling point. Allyl chloride has a sp. gr. of 0·9340 at 0°, and boils at 44°–45°. The isomeric compound chloropropylene has a sp. gr. of 0·9307 at 0°, and boils at 25·5°. The latter, when heated to 120° with sodium ethylate, is converted into allylene, but allyl chloride is converted by alcoholic potash-solution, even below 100°, into allyl-ethylic ether. The hydrogen in the allyl compounds appears to be more intimately united with the carbon than in the propylene compounds (Oppenheim).

Allyl trichloride, $C^3H^5Cl^3$, prepared by passing chlorine gas into allyl iodide covered with a layer of water, or by digesting the iodide with potassium bichromate and hydrochloric acid, is a colourless liquid having the odour of chloral, and not solidifying at $-10°$; sp. gr. $=$ 1·41 at 0°. Boiling point between 154° and 157°, like that of the isomeric (or identical) compound, trichlorhydrin. It is not converted into allylene by potash or by sodium ethylate (Oppenheim, *Bull. Soc. Chim.* [2] ii. 97).

ALLYL IODIDE, C^3H^5I, is produced by slowly distilling a mixture of allyl alcohol, iodine, and red phosphorus. As soon as the allyl iodide has passed over, water must be added to distil off the residue; otherwise there will be danger of an explosion (Tollens a. Henninger, *Bull. Soc. Chim.* [2] xi. 396). Also by distilling glycerin in excess with hydriodic acid:

$$C^3H^5(OH)^3 + 3HI = C^3H^5I + 3H^2O + I^2.$$

If, on the other hand, the hydriodic acid is in excess, the chief product is isopropyl iodide (v. 800):

$$C^3H^5(OH)^3 + 5HI = C^3H^7I + 3H^2O + 2I^2$$

(Erlenmeyer, *Jahresb.* 1861, p. 667; 1866, p. 524). *Hydriodic acid gas* passed into allyl iodide converts it into isopropyl iodide, with separation of iodine: $C^3H^5I + 2HI = C^3H^7I + I^2$ (M. Simpson, *Proc. Roy. Soc.* xii. 533). Allyl iodide treated at ordinary temperatures with *zinc*, *hydrochloric acid*, and *alcohol*, yields propylene gas (Tollens a. Henninger). Heated to 100° in a sealed tube with *zinc-ethyl*, it yields diallyl, C^6H^{10}, amylene, C^5H^{10}, and amyl hydride, C^5H^{12}. The formation of amylene is represented by the equation $C^3H^5 + C^2H^5 = C^5H^{10}$, and that of amyl hydride probably by the equation

$$\underset{\substack{\text{Allyl-}\\\text{iodide.}}}{2C^3H^5I} + \underset{\text{Zinc ethyl.}}{Zn(C^2H^5)^2} = ZnI^2 + \underset{\substack{\text{Amyl}\\\text{hydride.}}}{C^5H^{12}} + \underset{\text{Allylene.}}{C^3H^4} + \underset{\text{Ethylene.}}{C^2H^4}$$

(Wurtz, *Compt. rend.* liv. 387). With *cacodyl*, allyl iodide forms cacodyl iodide, $As'''(CH^3)^2I$ (arsenious iododimethide), and crystals of arsenic iodo-dimethyl-diallylide, $As^v(CH^3)^2(C^3H^5)^2I$, which when treated with moist silver oxide is converted into the strongly caustic alkaline base $As^v(CH^3)^2(C^3H^5)^2(OH)$ (Cahours, *Ann. Ch. Phys.* [3] lxii. 291).

The chloride, bromide, and iodide of allyl exhibit differences of boiling point nearly equal to those observed in the corresponding ethyl compounds; thus:

$$\begin{array}{lccccccccc} & \text{Chloride.} & & & & \text{Bromide.} & & & & \text{Iodide.} \\ \text{Allyl} & 44{\cdot}5^\circ & — & 25{\cdot}5^\circ & — & 70^\circ & — & 31^\circ & — & 101^\circ \\ & | & & & & | & & & & | \\ & 32{\cdot}5^\circ & & & & 30^\circ & & & & 29^\circ \\ & | & & & & | & & & & | \\ \text{Ethyl} & 12^\circ & — & 28^\circ & — & 40^\circ & — & 32^\circ & — & 72^\circ \end{array}$$

On the boiling points of allyl compounds, see also Oppenheim (*Zeitschr. f. Chem.* [2] v. 344); Tollens (*ibid.*).

Allyl Iododichloride, $C^3H^5ICl^2$, is produced by the action of iodine monochloride on allyl iodide:

$$C^3H^5I + 2ICl = C^3H^5ICl^2 + I^2.$$

When purified by washing with dilute potash, distilling, and collecting the portion which passes over between 205° and 210°, it forms a colourless oil, insoluble in water, and having a sweet but biting taste (M. Simpson, *Proc. Roy. Soc.* xiii. 540).

Diallyl Compounds.

Diallyl, C^6H^{10}, or *Allyl in the free state*, was first obtained by Berthelot a. De Luca (i. 140) by treating allyl iodide with sodium. It is also produced: 1. Together with other hydrocarbons, by the action of allyl iodide on zinc-ethyl (Wurtz, *Compt. rend.* liv. 387; lvi. 354).—2. By treating allyl iodide with a pulverised alloy of 2 pts. tin and 1 pt. sodium. The action, which begins in the cold, is ultimately assisted by heat, and the crude hydrocarbon thus obtained is purified by heating it for a few hours with sodium, and distilling (Wurtz a. Leclanché, *Ann. Ch. Phys.* [4] iii. 120).—3. By reducing allyl iodide with iron (Linnemann, *Bull. Soc. Chim.* [2] vii. 424).—4. By dry distillation of mercurallyl iodide (prepared by agitating crude allyl iodide with mercury and a small quantity of iodine):

$$(C^3H^5)^2Hg^2I^2 = C^6H^{10} + HgI^2 + Hg.$$

The diallyl which passes over is purified by repeated rectification over sodium (Linnemann, *Ann. Ch. Pharm.* cxl. 180).

Diallyl is a pungent ethereal liquid boiling at 58° (Wurtz, Buff); sp. gr. = 0·681 at 0°, 0·688 at 17°, 0·6454 to 0·6459 at 58° (Buff, *Ann. Ch. Pharm. Suppl.* iv. 145). Vapour density, obs. = 2·92, calc. = 2·84. It dissolves in strong sulphuric acid, with evolution of heat, the solution on cooling depositing a hydrocarbon differing from diallyl. According to Schorlemmer (*Ann. Ch. Pharm.* cxxxix. 240), it forms with sulphuric acid a pitchy mass, together with hydrocarbons of the series C^nH^{2n-2}, analogous to those obtained from coal-naphtha.

Diallyl belongs to the series C^nH^{2n-2}, but is not a true homologue of acetylene and allylene, because its boiling point is lower than that of hexylene, C^6H^{12}, whereas the boiling points of acetylene and allylene are above those of the corresponding olefines. Like all the hydrocarbons of the series, it is bivalent and quadrivalent, forming two groups of compounds containing respectively 2 and 4 atoms of univalent radicles.

I. Diallyl Compounds containing Two Atoms of Univalent Radicles (Wurtz, *Ann. Ch. Phys.* [4] iii. 129; *Jahresb.* 1862, p. 493; 1864, p. 511).—*Diallyl monohydrochloride*, $C^6H^{10}.HCl$, is produced, together with the dihydrochloride, by the action of hydrochloric acid upon diallyl. It is a liquid heavier than water, having a faint aromatic odour, boiling at 130°-140°.

Monohydriodide. $C^6H^{10}.HI$.—Produced: 1. Together with the dihydriodide (*q.v.*), by the action of hydriodic acid upon diallyl. 2. Together with diallyl, by the action of alcoholic potash on the dihydriodide. Colourless liquid, of sp. gr. 1·497 at 0°, boiling at 164° to 166°. Treated for twenty-four hours with moist silver oxide, it yields, (1) diallyl and hexylene; (2) a liquid boiling at 130°–140°, and probably identical with diallyl alcohol; (3) a liquid boiling at 180°, the ether of the same alcohol, $(C^6H^{10}.H)^2O$.

Monoacetate. $C^6H^{10}.H.C^2H^3O^2$.—Produced in the preparation of the diacetate, and contained in the liquid which distils at 110°–160°. When purified by washing with sodium carbonate, drying, and fractional distillation, it is a colourless aromatic liquid, insoluble in water, of sp. gr. 0·912 at 0°, boiling at 150°–160°. Slowly decomposed by strong boiling potash-ley, more quickly by distillation over solid potassium hydrate. Does not unite with acetic acid when heated with it to 140°.

Diallyl Monohydrate, $C^6H^{10}.H^2O$, or *Pseudo-hexylene Oxide*, $(C^6H^{12})''O$.—This is the chief product of the action of moist silver oxide on allyl dihydriodide (*infra*). It is a colourless mobile liquid, insoluble in water, having a very pungent odour, a sp. gr. of 0·8387 at 0°, boiling at 92°–95°. It is strongly attacked by *hydriodic acid* in concentrated aqueous solution, producing a mixture of diallyl dihydriodide, $C^6H^{10}.H^2I^2$, and a body isomeric or identical with hexylene iodhydrin, $C^6H^{12}\left\{\begin{matrix}OH\\I\end{matrix}\right.$, the latter being formed by direct combination. Heated with *acetic anhydride*, it yields a small quantity of diallyl diacetate, $C^6H^{12}O(C^2H^3O)^2O$, or $C^6H^{10}.H^2.(C^2H^3O^2)^2$. According to these two reactions, the compound may be regarded as pseudohexylenic oxide.

Diallyl Alcohol. $C^6H^{10}\left\{\begin{matrix}H\\OH\end{matrix}\right.$.—This compound, isomeric with the last, is produced by treating the monoacetate with solid potash, and is also found among the products of the action of moist silver oxide on the dihydriodide. It is a liquid, insoluble in water, having an aromatic odour, a sp. gr. of 0·8604 to 0·8625 at 0°, and boiling at about 140°. With strong aqueous hydriodic acid it becomes hot, and forms a mixture which, when heated to 100°, yields diallyl dihydriodide.

II. Diallyl Compounds containing Four Atoms of Univalent Radicles.—A few of these compounds were obtained by Berthelot a. De Luca; the rest have been discovered and investigated by Wurtz (*loc. cit.*). The *tetrabromide*, $C^6H^{10}Br^4$, and *tetraiodide*, $C^6H^{10}I^4$, discovered by Berthelot a. De Luca, were originally regarded as allyl dibromide and di-iodide, $C^3H^5Br^2$ and $C^3H^5I^2$ (i. 141, 142). *Diallyl Tetranitrylide*, $C^6H^{10}(NO^2)^4$, is formed in white crystals on passing nitrogen tetroxide, N^2O^4, into a solution of diallyl in anhydrous ether cooled with ice and salt (L. Henry).

Dihydrochloride. $C^6H^{10}.H^2Cl^2$. — Produced, together with the monohydrochloride, by heating diallyl for six or eight hours with fuming hydrochloric acid. The upper layer of liquid thereby produced, yields by fractional distillation, monohydrochloride at 130°–140°, and dihydrochloride at 170°–180°. The latter is also produced by heating the monohydrate or dihydrate of diallyl with strong hydrochloric acid. It is a colourless, heavy liquid, insoluble in water (Wurtz).

A *diallylic dichlorhydrin*, $C^6H^{10}\left\{\begin{matrix}Cl^2\\(OH)^2\end{matrix}\right.$, is produced by the combination of hypochlorous acid with diallyl. The two bodies unite readily, and with considerable evolution of heat, the diallyl, which is lighter than water, being converted into a heavy oil which sinks to the bottom (L. Henry, *Zeitschr. f. Chem.* [2] v. 479).

Dihydriodide. $C^6H^{10}.H^2I^2$.—Prepared by heating diallyl in a strong sealed flask for five or six hours with excess of highly concentrated hydriodic acid, and purified by washing with alkaline water, drying over calcium chloride, and heating in a vacuum to 130°–140°, whereupon diallyl and the monohydriodide distil over, and pure dihydriodide remains. It is a transparent amber-yellow liquid, insoluble in water, of sp. gr. 2·024 at 0°, does not decompose or volatilise in a vacuum at 140°, but gives off iodine at a higher temperature. Treated with *sodium*, or, better, with an alloy of sodium and tin rich in sodium, it is converted partly into hexylene:

$$C^6H^{10}.H^2I^2 + Na^2 = 2NaI + C^6H^{12};$$

partly into diallyl monohydriodide:

$$2(C^6H^{10}.H^2I^2) + Na^2 = 2(C^6H^{10}.HI) + 2NaI + H^2,$$

the monohydriodide being at the same time resolved into several hydrocarbons of higher boiling point, among which is found the compound $C^{12}H^{22}$, boiling between 190° and 200°: $2(C^6H^{10}.HI) + Na^2 = 2NaI + C^{12}H^{22}$. In contact with *alcoholic potash*, the dihydriodide is immediately decomposed, with formation of potassium iodide, diallyl, and the monohydriodide, the two latter distilling over with water:

$$C^6H^{10}.H^2I^2 + KHO = H^2O + KI + C^6H^{10}.HI$$

and

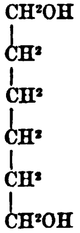
$$C^6H^{10}.H^2I^2 + 2KHO = 2H^2O + 2KI + C^6H^{10}.$$

Diacetate. $C^6H^{10}.H^2.(C^2H^3O^2)^2$.—Formed, together with other products, by treating finely divided silver acetate suspended in ether with an equivalent quantity of diallyl dihydriodide for twenty-four hours at ordinary temperatures. On distilling the filtered ethereal liquid, ether and a little diallyl pass over first; then, between 110° and 180°, acetic acid and diallyl monoacetate; afterwards diallyl hydroacetate, $C^6H^{10}.H^2\left\{\begin{matrix}C^2H^3O^2\\OH\end{matrix}\right.$, boiling at about 210°; and lastly diallyl diacetate, boiling at 225°–230°. The latter is a thick colourless oil, having a slightly aromatic odour, insoluble in water, and having density of 1·009 at 0°. It is decomposed by potassium hydrate, yielding diallyl dihydrate (Wurtz).

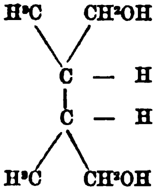
Diallyl Dihydrate or *Pseudohexylene Glycol*, $C^6H^{14}O^2 = C^6H^{10}\left\{\begin{matrix}H^2\\(OH)^2\end{matrix}\right. = C^6H^{12}(OH)^2$, is obtained by decomposing diallyl diacetate, or the crude product of the preparation of that compound distilling between 190° and 230°, with a quantity of recently calcined and pulverised potassium hydrate, just sufficient to saponify the diacetate. Only half this quantity is however added at first, and the mixture, after having been heated for a short time, is distilled in an oil-bath at 300°. The distillate is rectified; the residual portion, boiling above 180°, is carefully treated with the remaining quantity of potash, added in two separate portions, till a distinct alkaline reaction is each time produced; and the product is rectified, the diallyl dihydrate passing over between 210° and 220°. It is a thick colourless syrup, having a sp. gr. of 0·9638 at 0°, and so expansible that its sp. gr. at 65° (referred to water at 0°) is only 0·9202. It boils between 212° and 215°, dissolves in water, alcohol, and ether, and does not decompose even at the boiling point of mercury. With *hydrochloric acid gas* it becomes hot without forming any new product; but when heated in a closed vessel with very strong aqueous *hydrochloric acid*, it forms diallyl dihydrochloride: $C^6H^{10}.H^2(OH)^2 + 2HCl = 2H^2O + C^6H^{10}.H^2Cl^2$. With concentrated *hydriodic acid* in like manner it forms diallyl dihydriodide (Wurtz).

Diallyl dihydrate is isomeric with normal hexylene glycol prepared by the usual series of reactions from hexylene (obtained from mannite, or from the hexyl hydride of American petroleum). Hexylene glycol, $C^6H^{12}(OH)^2$, boils at 215°–220°, that is to say, 10° lower than diallyl-dihydrate; and hexylene diacetate, $C^6H^{12}(C^2H^3O^2)^2$, boils at 207°, or from 5° to 7° lower than diallyl diacetate.

The isomerism between normal hexylene glycol and diallyl dihydrate or pseudohexylene glycol may be represented by the following formulæ:



Hexylene glycol.



Diallyl dihydrate.

or $(C^6H^{12})''\left\{\begin{matrix}OH\\OH\end{matrix}\right.$ $(C^6H^{10})^{iv}\left\{\begin{matrix}H^2\\(OH)^2.\end{matrix}\right.$

ALLYLAMINE. $(C^3H^5)H^2N$.—This base, discovered by Cahours and Hofmann, who obtained it by distilling allyl cyanate with potash (i. 146), is likewise produced by the action of zinc and hydrochloric acid on an alkaline solution of allyl sulphocyanate (mustard oil) free from cyanate:

$$(C^3H^5)CNS + 2H^2O = (C^3H^5)H^2N + H^2S + CO^2.$$

The acid solution freed from alcohol yields with potash a distillate, which, when neutralised with hydrochloric acid, first deposits crystals of sal-ammoniac, and afterwards deliquescent crystals of allylamine hydrochloride, soluble in strong alcohol. The base, C^3H^7N, separated from this salt by distillation with potash, forms a colourless, rather mobile liquid, having a burning, sharp taste and a pungent, ammoniacal, faintly alliaceous odour, which excites sneezing and lachrymation. Boiling point 58°; sp. gr. = 0·864 at 15°. Burns with bright flame; mixes in all proportions with water, producing rise of temperature; has a strong alkaline reaction, and precipitates aluminic, ferric, mercuric, cupric, and argentic salts, the precipitates formed in the last two cases being soluble in excess of allylamine. *Sulphate of allylamine* forms feathery crystalline aggregates, permanent in the air. The *platino-chloride*, $C^3H^8NPtCl^6$, crystallises in orange-yellow monoclinic prisms flattened out into plates (C. Oeser, *Ann. Ch. Pharm.* cxxxiv. 7).

Dimonochlorallylamine, $C^6H^9Cl^2N = \left.\begin{matrix} C^3H^4Cl \\ C^3H^4Cl \\ H \end{matrix}\right\} N$, is produced, together with sal-ammoniac, by heating trichlorhydrin, mixed with 7 or 8 vol. alcohol and saturated with ammonia gas, to 130°–140° under pressure for a few days. The product is saturated with hydrochloric acid, and the hydrochloride of dimonochlorallylamine is dissolved out by alsolute alcohol. The base separated from this salt by potash is an oil boiling at about 194°, heavier than water, slightly soluble therein, very soluble in alcohol and ether. The aqueous solution contains enough of the base to precipitate copper and silver salts. The base emits vapours even at ordinary temperatures. The *hydrochloride*, $N(C^3H^4Cl)^2H^2Cl$, is soluble in water and alcohol, and separates from the latter in a mass of small deliquescent needles fusible below 100°. The *platinochloride*, $[N(C^3H^4Cl)^2HCl]^2.PtCl^4$, is a yellow crystalline precipitate, soluble in water, slightly soluble in alcohol, insoluble in ether (C. Engler, *Bull. Soc. Chim.* [2] ix. 134).

Dimonochlorallylethylamine, $N(C^3H^4Cl)^2(C^2H^5)$, is formed by heating the preceding base to 100° in sealed tubes with a large excess of ethyl iodide. Separated by potash from the resulting hydriodide, it forms an oil boiling at a little above 200°, in other respects resembling the preceding. Its *hydrochloride* also has the aspect of that of dimonochlorallylamine, but it is much less soluble in water and in alcohol. The *platinochloride*, $[N(C^3H^4Cl)^2C^2H^5.HCl]^2PtCl^4$, is crystalline. The base treated with ethyl iodide yields a crystalline mass, probably consisting of $[N(C^3H^4Cl)^2(C^2H^5)^2I$ (Engler, *loc. cit.*).

ALLYL-ANILINE, $N(C^6H^5)(C^3H^5)H$, is produced by the action of allyl iodide on aniline (iv. 449).

ALLYLENE. C^3H^4.—This hydrocarbon was discovered by Sawitsch (*Compt. rend.* lii. 399), who obtained it by the action of sodium ethylate on monobromopropylene:

$$C^3H^5Br + NaOC^2H^5 = C^3H^4 + C^2H^6O + NaBr.$$

For the mode of preparation see Appendix to vol. i. (p. 1112). It may be obtained in like manner by the action of sodium ethylate on monochloropropylene, C^3H^5Cl, produced by treating acetone with phosphorus pentachloride (Friedel, *Bull. Soc. Chim.* 1864, ii. 96). It likewise results from the action of sodium on the dichloride of dichloracetone (or allylene tetrachloride), $C^3H^4Cl^4$ (Borsche a. Fittig, *Ann. Ch. Pharm.* cxxxiii. 111), and on glycidic dichloride or tetrachloride, $C^3H^4Cl^2$ and $C\,H^4Cl^4$ (Pfeffer and Fittig, *ibid.* cxxxv. 257). The reaction in either case is very violent, and, to avoid explosion, it is necessary to mix the chlorine-compound with five or six times its volume of neutral hydrocarbons boiling at 100°–120° (obtained by rectification of commercial benzol and purified by distillation from sodium). The mixture is gently heated, and the gaseous allylene which is given off is absorbed by an ammoniacal solution of cuprous chloride, from which it is separated by treating the resulting cuprous allylenide with dilute hydrochloric acid.

Allylene is a colourless gas, having an unpleasant odour, and burning with a bright and very smoky flame. It is very soluble in alcohol, and dissolves in water readily enough to render it necessary to add common salt to the water over which it is to be collected. With an ammoniacal solution of *cuprous chloride* it forms a canary-yellow precipitate; with *mercurous nitrate*, a dark-grey precipitate, which decomposes without detonation when heated; with *silver nitrate*, a white precipitate, which is decomposed by heat, with explosion and production of a reddish flame. Allylene gently heated with *sodium* is partly decomposed, with formation of acetylene-sodium, separation of charcoal, and increase of the gaseous volume:

$$C^3H^4 + Na^2 = C^2Na^2 + C + 2H^2.$$

The residual gas contains a small quantity of propylene (Berthelot, *Jahresb.* 1866, p. 524). Allylene is absorbed easily and in large quantity by strong *sulphuric acid*, and may be thereby distinguished from acetylene, which is but slowly absorbed by sulphuric acid (Berthelot).

Allylene differs from the saturated hydrocarbon, propane or propyl hydride, C^3H^8, by 4 atoms of hydrogen, and therefore acts as a quadrivalent radicle, taking 4 at. Br, Cl, &c., to form saturated compounds; but it can also form unsaturated compounds by combination with 2 at. of a univalent radicle, or 1 at. of a bivalent radicle.

In Hofmann's systematic nomenclature of hydrocarbons (*Proc. Roy. Soc.* xv. 57) allylene is designated as propine:

$$\underset{\text{Propane.}}{C^3H^8} \qquad \underset{\text{Propene.}}{(C^3H^6)''} \qquad \underset{\text{Propine.}}{(C^3H^4)''''}$$

Bromine-compounds of Allylene (Oppenheim, *Bull. Soc. Chim.* [2] ii. 6; iv. 434).—When allylene is acted upon in the shade by bromine, added in drops or brought in contact with it in the state of vapour, a transparent liquid is formed, which is a mixture of the two bromine-compounds, $C^3H^4Br^2$ and $C^3H^4Br^4$; if, on the other hand, the action takes place in sunshine, hydrobromic acid is evolved, and a black, partially carbonised liquid is produced. The compounds formed in the shade may be separated by distillation in a vacuum.

Allylene dibromide, $C^3H^4Br^2$, is a colourless, sweetish liquid, the vapour of which excites a copious flow of tears. Sp. gr. = 2·05 at 0°. It boils in the air without decomposition between 126° and 138°, the greater part distilling over at 132°. It is thereby distinguished from glycidic dibromide or epibromhydrin (ii. 899), which boils at 151°–152°, and from dibromopropylene, which boils at 120°. It unites with bromine in the shade without elimination of hydrobromic acid.

Allylene tetrabromide, $C^3H^4Br^4$, the chief product of the action of bromine on allylene, is a colourless liquid having an odour of camphor and a sp. gr. of 2·94 at 0°. Under a pressure of 1 centimetre it distils almost completely between 110° and 130°, and under the ordinary atmospheric pressure it boils, with evolution of hydrobromic acid, between 225° and 230°, that is to say, nearly at the same temperature as dibromopropylene dibromide, $C^3H^4Br^2.Br^2$ (226° according to Cahours). Mercury does not act upon it at 100°, but carbonises it completely at 130°. Heated with an alcoholic solution of potassium acetate, it decomposes in the manner shown by the equation:

$$\underset{\substack{\text{Allylene}\\\text{tetrabromide.}}}{C^3H^4Br^4} + \underset{\substack{\text{Potassium}\\\text{acetate.}}}{\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O} + \underset{\text{Alcohol.}}{\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O} = \underset{\substack{\text{Tribromo-}\\\text{propylene.}}}{C^3H^3Br^3} + KBr + \underset{\substack{\text{Ethyl}\\\text{acetate.}}}{\left.\begin{matrix}C^2H^3O\\C^2H^5\end{matrix}\right\}O} + H^2O.$$

Tribromopropylene, the chief product of this reaction, is a very stable, colourless liquid, which boils between 183° and 185°, and is thereby distinguished from the isomeric bromallylene bromide, $C^3H^3Br.Br^2$, which Liebermann has obtained by the action of bromine on argentic allylene (*infra*), this latter compound being completely decomposed by boiling.

Iodine-compounds of Allylene. *Allylene di-iodide*, $C^3H^4I^2$, is most easily obtained by exposing allylene for two months to the action of a solution of iodine in potassium iodide, in bottles filled with the liquid and exposed to sunshine. After washing with potash it forms a slightly coloured oil, boiling at 198°, and having a sp. gr. of 2·62 at 0°. It turns brown when exposed to light, and is slowly attacked by acetate and oxalate of silver. With an alcoholic solution of potassium acetate it yields allylene and ethyl acetate (Oppenheim, *Bull. Soc. Chim.* [2] iv. 434).

Allylene dihydriodide, $C^3H^4.H^2I^2$, isomeric with propylene di-iodide, is produced by direct combination of allylene with concentrated hydriodic acid (Oppenheim, *loc. cit.*; Semenoff, *ibid.* [2] v. 446). It is a heavy, peculiar-smelling oil, having a sp. gr. of 2·15 at 0° (Oppenheim), 2·448 at 0° (Semenoff). Boils with decomposition between 147° and 148°, but may be easily distilled in a current of steam or of any indifferent gas. It becomes coloured by exposure to air or light, dissolves sparingly in alcohol, easily in ether (Semenoff).

The *monohydriodide*, $C^3H^4.HI$, isomeric with allyl iodide, cannot be obtained by direct combination, but is produced by treating the dihydriodide with an equivalent quantity of potash in alcoholic solution, and mixing the distillate with water. It is a colourless, strongly refracting liquid, scarcely coloured by light, and having a strong, but agreeable odour. It boils at 82° (Semenoff), 93°–103° (Oppenheim), and has a sp. gr. of 1·8346 at 0°, or 1·8028 at 16° (Semenoff).

Chlorine-compounds. The chlorine-compounds of allylene have not been formed by direct combination, but compounds isomeric, or perhaps identical, with them have been obtained from other sources. Thus Borsche and Fittig (*Ann. Ch. Pharm.* cxxxxiii. 111 ; *Jahresb.* 1865, p. 313) by treating acetone with chlorine have obtained compounds containing $C^3H^4Cl^2$ and $C^3H^4Cl^4$, the former boiling at 120° and the latter at 153°. The latter is identical with Linnemann's dichloracetone dichloride (p. 27). By treating glycidic dichlorhydrin (epidichlorhydrin), $C^3H^4Cl^2$ (ii. 899), with chlorine, the same chemists have obtained the compound $C^3H^4Cl^4$, isomeric with the preceding, and distilling at 164°. Hübner a. Geuther (*Ann. Ch. Pharm.* cxiv. 36), by treating acrolein with phosphorus pentachloride, have obtained a compound, $C^3H^4Cl^2$, which they designate as allylene dichloride. When purified by washing with water, desiccation with calcium chloride, and rectification, it is a colourless oil of sp. gr. 1·17 at 27·5°, having a sweetish ethereal odour, like that of chloroform, and boiling at 84·4°. It is distinguished from epichlorhydrin by not being acted upon by sodium. Another body having the same composition appears to be formed at the same time.

By heating 1 molecule of the chloride just mentioned with 2 molecules of silver acetate, Hübner and Geuther have obtained a compound which they regard as allylene diacetate:

$$C^3H^4Cl^2 + 2AgC^2H^3O^2 = 2AgCl + C^3H^4(C^2H^3O^2)^2.$$

The same compound is obtained by heating equivalent quantities of acrolein and acetic anhydride in closed vessels. It is a colourless liquid, having an acrid taste and fishy odour; sp. gr. = 1·076 at 22°; distilling at about 130°. It slowly reduces an ammoniacal solution of silver nitrate, and when heated with potash yields potassium acetate and acrolein.

Substitution-derivatives of Allylene.

Argentallylene, C^3H^3Ag, is produced by the action of allylene on an ammoniacal solution of silver nitrate, as a very light white precipitate, altering like silver chloride when exposed to light. Acids decompose it, reproducing allylene. When thrown on bromine or on phosphoric or antimonic chloride, it takes fire, and burns with a hissing noise. It may be dried between 60° and 70°, and detonates at about 150° without previous fusion, but with separation of spongy charcoal (Liebermann, *Ann. Ch. Pharm.* cxxxv. 266). According to Sawitsch, on the contrary, it explodes when heated, with production of flame. It is attacked by a solution of sal-ammoniac, forming a liquid which decomposes on boiling into allylene and silver chloride:

$$C^3H^3Ag + NH^4Cl = AgCl + C^3H^4 + NH^3$$

(Berthelot, *Jahresb.* 1866, p. 523).

'The precipitates formed by allylene in solutions of other metallic salts appear to be analogous in composition to those formed in the same solutions by acetylene (p. 35), the copper-compound, for example, consisting of cuprosallyl oxide, $(C^3H^3Cu^2)^2O$; they are, however, much more unstable than the acetylene compounds. Berthelot thinks it probable that the precipitate formed by allylene in ammoniacal silver nitrate may consist in the first instance of argentallyl oxide, $(C^3H^3Ag^2)^2O$, which quickly changes into argentallylene.

Iodallylene, C^3H^3I, is formed by gently heating argentallylene with a solution of iodine in potassium iodide, and passes over with the aqueous vapour as an oily body, having nearly the sp. gr. of 1·7, and boiling at 98°. It has a pungent odour, attacks the eyes and the mucous membranes, dissolves easily in ether, scarcely at all in alcohol, slightly in water, but easily in acetic acid, from which it is precipitated by water in its original state. It is not attacked by potash-ley, sodium, or sodium ethylate; but by *zinc* and *hydrochloric acid* or by *zinc-amalgam*, it is decomposed with separation of allylene. *Bromine* cautiously added to cooled iodallylene unites with it, forming the dibromide, $C^3H^3I.Br^2$, a heavy oil which turns yellow when exposed to light. The di-iodide, $C^2H^3I.I^2$, may also be formed by direct combination, but more easily by agitating dry argentallylene with an ethereal solution of iodine till the colour disappears, and then adding another equal quantity of iodine. The product is then left to itself for a week, the excess of iodine removed by agitation with dilute potash, the ethereal solution evaporated, and the remaining crystals of diallylene-diiodide washed with a little ether. The di-iodide, when crystallised slowly and in the dark, forms colourless lancet-shaped needles, often half an inch long. It is very sensitive to light; may be dried over calcium chloride, but not over oil of vitriol; melts at 64°; decomposes at about 78°; and dissolves easily in ether and in chloroform, less easily in benzene, and still less in alcohol. Heated with pulverised potassium hydrate, it is reconverted into iodallylene (Liebermann, *loc. cit.*).

Bromallylene, C^3H^3Br, **and products derived from it.** *Bromallylene dibromide*, $C^3H^3Br^3 = C^3H^3Br.Br^2$, is produced by adding bromine to argentallylene (not previously dried) suspended in water, and passes over on distillation, together with the aqueous vapour. It is an oily body, which decomposes when distilled alone, yielding hydrobromic acid and allylene bromide, $C^3H^4Br^2$ (?).

Bromallylene, C^3H^3Br, is formed (together with $C^3H^4Br^2$) when allyl tribromide, $C^3H^5Br^3$, or its isomeride, bromopropylene dibromide, $C^3H^5Br.Br^2$, is treated with a considerable quantity of alcoholic potash. By the further action of the alcoholic potash—which acts like potassium ethylate, replacing the bromine by oxethyl—bromallylene is converted into oxethyl-allylene, $C^3H^3(OC^2H^5)$ or $\left.\begin{matrix}C^3H^3\\C^2H^5\end{matrix}\right\}O$:

$$C^3H^3Br + KOC^2H^5 = KBr + C^3H^3OC^2H^5.$$

The univalent radicle C^3H^3 is called by Liebermann propargyl, and the ethereal compound just mentioned is accordingly designated as propargyl ethylate or ethyl propargylate.*

This ether can exchange an atom of hydrogen belonging to the propargyl for silver, forming ethyl argentopropargylate or argentopropargyl ethylate, $C^3H^2Ag(OC^2H^5)$, which is obtained by heating allyl tribromide for a long time with alcoholic potash, then distilling off the alcohol, diluting with water to separate a brominated oil, and pouring the aqueous solution into ammoniacal silver nitrate. The silver-compound then separates as a dazzling white bulky precipitate, which presents no appearance of crystallisation. On the approach of a flame it melts, explodes, and leaves a residue which burns in contact with the air, leaving metallic silver. Acids abstract the silver and convert the compound into ethyl propargylate or oxethyl-allylene, $C^3H^3(OC^2H^5)$. The pure ether thus prepared boils at 72°. Like allylene itself, it unites directly with iodine, forms a yellow precipitate with ammoniacal cuprous chloride, and with ammoniacal silver nitrate a precipitate identical with the silver-compound above described.

Ethyl argentopropargylate or oxethyl-argentallylene, $C^3H^2Ag(OC^2H^5)$, reacts with iodine and bromine in the same manner as argentallylene itself, taking up an atom of iodine in place of silver, and forming the compound $C^3H^2I(OC^2H^5)$ or $\left.\begin{matrix}C^3H^2I\\C^2H^5\end{matrix}\right\}O$, which again can take up iodine and bromine, forming the compounds $C^3H^2I(OC^2H^5).I^2$ and $C^3H^2I(OC^2H^5).Br^2$.

Methyl propargylate or propargyl methylate, $C^3H^3(OCH^3)$ or $\left.\begin{matrix}C^3H^3\\CH^3\end{matrix}\right\}O$, is produced by boiling tribromallyl with a solution of potash in methyl alcohol. It forms with ammoniacal silver nitrate a lemon-yellow precipitate, consisting of $C^3H^2Ag(OCH^3)$, from which the pure ether may be obtained by treatment with acids. This silver-compound distilled with a solution of iodine in potassium iodide yields the compound $C^3H^2I(OCH^3)$, which passes over as an oil, and solidifies at a low temperature in fine needles, but does not resume the liquid state till heated to 12° (Liebermann).

Propylphycite, $C^3H^8O^4$, the tetratomic alcohol which Carius obtained by combining epichlorhydrin, $C^3H^5\left\{\begin{matrix}O\\Cl\end{matrix}\right.$, with hypochlorous acid, ClHO, and treating the resulting compound, $(C^3H^4)^{iv}\left\{\begin{matrix}(OH)^2\\Cl^2\end{matrix}\right.$, with potash (v. 893), is perhaps identical with allylene alcohol, $(C^3H^4)^{iv}(OH)^4$.

ALLYL-ETHYL. $C^5H^{10} = C^3H^5.C^2H^5$.—A hydrocarbon, isomeric with amylene, produced by the action of allyl-iodide on zinc-ethyl. (See **AMYLENE.**)

ALLYL-ETHYLIC OXIDE. $\left.\begin{matrix}C^3H^5\\C^2H^5\end{matrix}\right\}O$.—This compound, produced by the action of ethyl iodide on potassium allylate (i. 142), and by that of alcoholic potash on allyl chloride (Oppenheim, *vid. sup.*), unites directly with bromine (like allyl alcohol), forming the compound $C^5H^{10}OBr^2$, which distils between 193° and 195°. It is a colourless liquid, which smells like dibromhydrin, becomes coloured when left to itself, and is partially decomposed by distillation. The corresponding chlorine-compound boils at 165°. The bromine-compound does not appear to be decomposed by zinc-methyl in ethereal solution. Sodium-amalgam withdraws the bromine, reproducing allyl-ethylic ether (Morkownikoff, *Jahresb.* 1865, p. 492).

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* It is isomeric with the pentatomic radicle propinyl, C^3H^3, derived from propane by abstraction of 5 atoms of hydrogen.

ALLYL-METHYL. $C^4H^8 = C^3H^5.CH^3$, isomeric with butylene (*q.v.*), is produced by the action of allyl-iodide on zinc-methyl (Wurtz).

ALOES. Of this drug there are two principal varieties, viz. a dark, opaque, liver-coloured variety called Aloë hepatica or liver-aloes, and a lighter kind, transparent in thin splinters, called Aloë lucida.

1. Liver-aloes is obtained most abundantly in Barbadoes, from *Aloë vulgaris*; it forms dry blackish lumps, having a dull fatty lustre, easily splitting into angular fragments, and yielding a brown-grey powder. A somewhat different Aloë hepatica is imported from Southern Arabia, by way of Bombay, and is hence called Indian or Bombay aloes. It is of a more brownish black, often indeed of a rather light liver-brown colour, breaks into large angular lumps, and yields a brownish to brownish-yellow or nearly orange-coloured powder.—2. Aloë lucida is produced in largest quantity near Algoa Bay, in the Cape Colony, chiefly from the species *Aloë spicata*, *A. africana*, *A. ferox*, and *A. lingua*; it is known in commerce as Aloë capensis and Aloë socotrina. The latter name is derived from the island Socotora, on the coast of Arabia, which was formerly the only source of this kind of aloes, but now yields little or none of it. Aloë lucida when dry forms a nearly uniform mass, having a strong vitreous lustre, translucent in small splinters, nearly black by reflected light, breaking very easily into broadly conchoïdal sharp-edged lumps, or into small reddish to light yellow-brown splinters, and yielding a light yellow powder.

All kinds of aloes have a peculiar odour, somewhat like that of myrrh and of saffron, and a bitter disagreeable taste. Pure aloes dissolves completely in alcohol, forming a clear solution; partly in cold water, almost completely in boiling water, liver-aloes however leaving a somewhat larger residue than the translucent variety. The opalescent yellow solution in a small quantity of hot water becomes turbid on the addition of more water, from separation of yellowish resinous drops, which on cooling cohere into a resinous deposit. The clear solution has a slight acid reaction, is coloured dark-brown by alkalis, black by ferric chloride, and forms a yellowish-grey precipitate with lead-acetate. Cold water dissolves about half the aloes, forming an acid solution which exhibits the same characters; it is not precipitated by alcohol, and is therefore free from gum (Flückiger, *Lehrbuch der Pharmakognosie des Pflanzenreichs*, Berlin, 1867).

From the experiments of Kosmann (*Bull. Soc. Chim.* 1863, p. 530), which were made upon Cape aloes, it appears that the portion of this drug which is soluble in water (the officinal *Extractum aloës*) and the insoluble portion (*resin of aloes*) have the same percentage composition, and are both resolvable by boiling with dilute sulphuric acid into glucose and several resinous bodies. He supposes that both these substances are formed, during the concentration of the juice, by oxidation and hydration of aloïn, the active principle existing in the laticiferous cellules of *Aloë spicata*:

$$\underset{\text{Aloïn.}}{3C^{17}H^{18}O^7} + O^3 + 6H^2O = \underset{\text{Soluble aloes.}}{3C^{17}H^{22}O^{10}} \text{ or } \underset{\text{Insoluble aloes.}}{C^{51}H^{66}O^{30}}$$

a. Soluble aloes is a yellow amorphous mass composed of agglomerated granules. By boiling with dilute sulphuric acid it is resolved into glucose (amounting to 15·8 per cent. of the soluble aloes) and two resinous acids, one of which, aloëresic acid, is precipitated, together with aloëretin, while the other, aloëretic acid, remains in solution:

$$\underset{\text{Soluble aloes.}}{6C^{17}H^{22}O^{10}} = \underset{\text{Aloëresic acid.}}{C^{30}H^{32}O^{14}} + \underset{\text{Aloëretic acid.}}{2C^{30}H^{34}O^{15}} + \underset{\text{Glucose.}}{2C^6H^{12}O^6} + 4H^2O.$$

and

$$\underset{\text{Aloëresic acid.}}{C^{30}H^{32}O^{14}} + O^{16} + 8H^2O = \underset{\text{Aloëretin.}}{C^{30}H^{48}O^{40}}$$

Aloëresic acid is insoluble in ether, has a yellowish-brown colour, and appears crystalline under the microscope. *Aloëretin*, which is insoluble in ether, is a brown, amorphous resin, not possessing acid properties. *Aloëretic acid*, which remains in solution together with the sugar, is separated by precipitating it with lead acetate, decomposing the precipitate with hydrogen sulphide, and treating the precipitated lead sulphide with alcohol. It forms a brown shining resin, composed of microscopic rhomboïdal tablets; is nearly insoluble in pure water and in ether, sparingly soluble in alcohol, more frequently in water containing sugar.

β. The portion of Cape aloes which is insoluble in water is yellow, soluble in alcohol, and remains, when the alcoholic solution is evaporated to dryness, in yellow, transparent, shining grains. By boiling with sulphuric acid in alcoholic solution it is resolved into glucose (amounting on the average to 16 per cent.), and a brown resin soluble in alcohol and in sodium carbonate, and separable by ether into aloëresinic acid, $C^{15}H^{16}O^{6}$, soluble, and aloëretinic acid, $C^{15}H^{18}O^{3}$, insoluble in that liquid. But these formulæ, as well as those of the products previously described, require confirmation.

According to Hlasiwetz (*Ann. Ch. Pharm.* cxxxiv. 287; cxxxvi. 31), aloes boiled with *dilute sulphuric acid* yields paracoumaric acid, $C^{9}H^{8}O^{3}$, from which by fusion with potassium hydrate, paraoxybenzoic acid, $C^{7}H^{6}O^{3}$, is obtained, as also, together with orcin, from aloes itself. Paracoumaric acid appears also to be formed, together with a small quantity of a fragrant volatile oil, a volatile fatty acid, and a volatile base, by boiling aloes with caustic soda-solution (Rochleder a. Czumpelick, *J. pr. Chem.* lxxxiv. 436; *Jahresb.* 1861, p. 743). Aloes heated with *nitric acid* is converted, first into aloetic acid, $C^{7}H^{2}N^{2}O^{5}$; then into chrysammic acid, $C^{7}H^{2}N^{2}O^{6}$; and finally into picric and oxalic acid. Robiquet, by distilling aloes with *quicklime*, obtained aloïsol (i. 148), a colourless or yellowish oil, smelling like amyl alcohol and bitter almond oil, and remaining liquid at −20°. Rembold (*Ann. Ch. Pharm.* cxxxviii. 186) obtained from aloes 1 per cent. of this oil, which he found to be a mixture of xylyl alcohol with acetone and hydrocarbons.

ALOETIC ACID. $C^{7}H^{2}N^{2}O^{5}$.—This acid, discovered by Schunck, and analysed by him and by Mulder (i. 148), with somewhat discordant results, has been further examined by Finck (*Ann. Ch. Pharm.* cxxxiv. 236), whose results differ from those of both the chemists just named. To prepare the acid, the mixture of chrysammic, aloetic, and a small quantity of picric acid, obtained as a green precipitate by treating aloes with nitric acid, as in Schunck's process, is digested with aqueous potassium acetate till the acetic acid is expelled; and the resulting potassium-salts are treated with cold water, which dissolves only the acetate: the resulting solution, mixed with barium acetate and evaporated, yields warty crystalline crusts of barium aloëtate, from which the aloetic acid may be separated by cold dilute nitric acid.

Aloetic acid thus obtained is a yellow amorphous powder consisting of $2C^{7}H^{2}N^{2}O^{5}.H^{2}O$. It dissolves sparingly in cold water, more easily in boiling water and in alcohol, forming purple-red solutions, which become yellow on addition of acids, and red again when neutralised. It has a strongly bitter and acrid taste, decomposes carbonates, and forms with the alkalis and alkaline earths, salts which dissolve in water with red colour; with other metallic oxides, sparingly soluble salts. The *silver salt* contains $C^{7}HAgN^{2}O^{5}$; the *barium salt* $C^{14}H^{2}Ba''N^{4}O^{10}$.

Aloetic acid is converted by boiling with nitric acid, first into chrysammic, then into picric acid. Digested with a solution of potassium or ammonium sulphide containing excess of alkali, it forms an indigo-blue, gelatinous substance, $C^{14}H^{8}N^{2}O^{7}$(?), slightly soluble in water, more soluble in alkalis.

ALOÏN. $C^{17}H^{18}O^{7}$.—This substance, the purgative principle of aloes, was first isolated by T. and H. Smith (*Chem. Gaz.* 1851, p. 107) from Barbadoes aloes. In *Aloë hepatica* it appears to exist wholly in the crystalline state; in other varieties partly amorphous, partly in an altered condition. Orlowski (*Zeitschr. anal. Chem.* v. 309) prepares it from *Aloë hepatica* [? Indian or Bombay aloes, p. 99] by dissolving the substance in 2 parts of water at 90°-95°, and leaving the clear decanted liquid to evaporate freely for ten or twelve days. The aloïn, which then separates as a dark-yellow granular mass, is pressed between filter-paper and further purified by crystallisation, first from water, then from alcohol. Barbadoes aloes is treated with only 1 part of water of the temperature above mentioned, the remaining fourth being added after cooling; the whole of the resin then separates after 12 hours. The decanted liquid is treated as above.

Aloïn treated with dilute sulphuric acid is resolved into glucose and rottlerin (Czumpelik, *Jahresb.* 1861, p. 743; Rochleder, *ibid.* 598):

$$\underset{\text{Aloïn.}}{C^{17}H^{18}O^{7}} + 2H^{2}O = \underset{\text{Glucose.}}{C^{6}H^{12}O^{6}} + \underset{\text{Rottlerin.}}{C^{11}H^{10}O^{3}}$$

According to Graebe a. Liebermann (*Zeitschr. f. Chem.* [2] iv. 503), aloïn treated with zinc-dust is converted into anthracene.

ALOSA MENHADEN, OIL OF. See MENHADEN OIL.

ALPHA-TOLUIC ACID, and its derivatives (v. 863).

ALPHA-USNIC ACID (v. 970).

ALPHA-XYLIC ACID (v. 1062).

ALSTONIA. The bark of *Alstonia constricta* (an apocycyaneous tree growing in Australia), which has a bitter taste and slight camphorous odour, contains, according to Palm (*Jahresb.* 1863, p. 615), a neutral resinous bitter principle (similar to cailcedrin and tulucunin), a volatile oil smelling like camphor, an iron-greening tannin, gum, resin, fat, wax, protein-substance, oxalic acid and citric acid. The ash, amounting to 6·06 per cent. of the bark, contains in 100 parts:

Na^2O	K^2O	$NaCl$	CaO	MgO	Fe^2O^3	Mn^3O^4	SO^3	P^2O^5	SiO^2	CO^2
0·48	6·96	3·06	32·83	3·61	3·43	0·78	9·33	trace	15·60	23·50.

ALSTONITE. *Bromlite.*—The orthorhombic variety of calcio-baric carbonate, $BaCO^3.CaCO^3$, found in the lead mines of Fallowfield in Northumberland, and Bromley Hill, near Alston, in Cumberland. The crystals, derived from a rhombic prism of 118° 50′, are double hexagonal prisms, resulting from the interpenetration of six octohedral crystals having a common vertical axis. Basal angles = 122° 30′ and 142°; re-entering angle = 178° 51′.

AMANDIN. An albuminous substance, contained, according to Commaille (*J. Pharm.* [4] iv. 108), in sweet almonds, and obtained by precipitating filtered almond milk with hydrochloric acid, dissolving the precipitate in alkaline water, and again precipitating with hydrochloric acid. Its acidulated solution forms with platinic chloride a precipitate containing 7·02 to 7·45 per cent. platinum. The solution in dilute hydrochloric acid also gives a precipitate with mercuric chloride.

AMARINE. $C^{21}H^{19}N^2$.—The sulphate of this base, obtained by direct combination, is described by Laurent (*Ann. Ch. Pharm.* lii. 359) as an acid salt; but according to a recent examination by P. Groth (*ibid.* clii. 122), it appears to be a neutral sulphate, having the composition $2(C^{21}H^9N^2)^2SO^4.7H^2O$. It is moderately soluble in water, and gives off its water of crystallisation between 100° and 110°; at 150° it becomes nearly insoluble in water, but does not lose weight. By recrystallisation it is obtained in monoclinic combinations, $\infty P \,.\, (\infty P\infty) \,.\, \infty P\infty \,.\, (P\infty) \,.\, oP$. Axes, $a : b : c$: 0·8537 : 1 : 0·8531. Angle of inclined axes = 97° 12·5′. Cleavage parallel to oP and $(P\infty)$. The plane of the optic axes is perpendicular to the plane of symmetry. Angle of optic axes for the red ray = 60° 33′ (Groth).

AMBRITE. $C^{16}H^{26}O^2$.—A fossil resin occurring in large lumps in the lignite formation of Drury and Hunua, in the province of Auckland, New Zealand. It is amorphous, with conchoïdal fracture, semitransparent, brittle, and of yellowish-grey colour. Hardness = 2; sp. gr. = 1·034. Burns with a yellow smoky flame; when heated on platinum-foil it gives off white fumes before melting, and then takes fire. Strongly electric when rubbed. Dissolves in carbon bisulphide, with separation of a white translucent amorphous mass; not in alcohol, ether, turpentine-oil, benzene or chloroform, even at the boiling heat. Fused with potash it turns brown, and floats on the surface as a viscid brown mass. By boiling for some hours with strong nitric acid, it is decomposed, the liquid becoming orange-red, and depositing on evaporation a yellow sticky mass, together with a few microscopic crystals. The ash contains iron, calcium, and sodium (v. Hauer a. Maly, *Jahresb.* 1866, p. 1034).

AMMONIA. *Preparation.*—Ammonia prepared from the commercial chloride or sulphate always contains small quantities of compound ammonias. To obtain it quite pure, it is necessary in the first instance to purify the salt from which it is to be evolved. Pure ammonium chloride may be obtained by boiling a saturated solution of commercial sal-ammoniac with $\frac{1}{10}$th vol. strong nitric acid, till chlorine is no longer evolved, redissolving the salt which crystallises out on cooling, and again heating this solution with $\frac{1}{20}$th vol. strong nitric acid. Pure ammonium sulphate is obtained by heating the commercial salt with $\frac{3}{4}$ths of its weight of strong sulphuric acid till decomposition commences, adding a small quantity of nitric acid, and heating the liquid till it is decolorised. The ammonia evolved from either of these pure salts by heating with calcium hydrate has merely a pungent odour, quite different from that of common ammonia.

Absolutely pure ammonia may also be obtained by digesting potassium nitrite (from 1 kilogr. saltpetre) with potash-ley, of sp. gr. 1·25 (15 litres), granulated zinc free from carbon[*] (3·5 kilogr.), and iron wire which has been ignited in the air and then reduced in a current of hydrogen (0·5 kils.), and finally distilling the mixture; or better—in order to avoid the rapid disengagement of hydrogen—decanting the liquid from the metal, and distilling it with gentle ebullition (Stas, *Zeitschr. anal. Chem.* vi. 423).

Liquefaction of Gaseous Ammonia.—Loir a. Drion (*Jahresb.* 1860, p. 41) liquefy ammonia gas by means of the cold (− 50°) produced by the rapid evaporation of liquid sulphurous oxide. A current of dry air is driven by the bellows of a glass-blower's lamp through several tubes at once into a quantity of liquid sulphurous oxide, in which is immersed the lower bend of a U-tube, traversed by a stream of ammonia gas. The liquefaction is accelerated by a slight increase of pressure.

The sp. gr. of liquid ammonia at 0° is 0·6362, referred to that of water at 0° (Andréeff, *Ann. Ch. Pharm.* cx. 1); according to Jolly (*ibid.* cxvii. 181), it is 0·6234 (mean of three observations). The volumes occupied at different temperatures are, according to Andréeff, as follows:—

Temp.	−10°	0°	+10°	+20°
Vols.	0·09805	1·000	1·0215	1·0450

The coefficient of expansion between −11° and 0° is, according to the mean of three observations by Jolly, 0·00155. It appears, then, that at temperatures sufficiently removed from its boiling point, liquid ammonia expands more than the gas.

Liquid ammonia boils under the ordinary pressure at −35·7° (Loir a. Drion), at −38·5° (Regnault).

The tension of ammonia vapour at various temperatures is, according to Regnault's latest determinations (*Rélation des Expériences*, &c.), as follows:—

Temp.	Tension in millimetres	Temp.	Tension in millimetres
−30°	866·09	+40°	11595·30
−20°	1392·13	50°	15158·33
−10°	2144·62	60°	19482·10
0°	3183·34	70°	24675·55
+10°	4574·03	80°	30843·09
20°	6387·78	90°	38109·22
33°	8700·97	100°	46608·24

Combustion of Ammonia.—The combustibility of ammonia in oxygen gas may be strikingly shown by passing a rapid stream of oxygen through boiling concentrated aqueous ammonia; the gas which issues from the mouth of the flask may then be set on fire, and burns with a greenish-yellow flame (Hofmann, *Chem. Soc. Qu. J.* xiii. 78). According to Heintz (*Ann. Ch. Pharm.* cxxx. 102), this experiment may be more safely made by passing a slow stream of oxygen into a flask filled to about ⅕th with ammonia, through a tube bent upwards at the end; this tube is introduced only a little way into the mouth of the flask before the gas is set on fire, and afterwards sunk deeper into the body of the flask; the flame then continues to burn quietly as long as a sufficient quantity of ammonia gas is supplied, exhibiting, in fact, a combustion of oxygen in an atmosphere of ammonia. The combustion of ammonia gas and oxygen may also be exhibited by means of a Daniell's jet. If a spiral of platinum wire 0·5 mm. thick, and attached to a long cork, be heated to redness, and suspended within a flask, of the capacity of about 450 cc., containing aqueous ammonia of 20 p. c., the cork lying loosely across the neck, and oxygen be passed into the liquid through a tube 10 mm. wide, the platinum spiral soon rises to a much brighter red heat, and the flask becomes filled, first with white fumes of ammonium nitrite, then with red fumes. If the ammonia be then warmed, the gaseous mixture takes fire with a sharp but not dangerous explosion; and the temperature of the platinum spiral is at the same time reduced below visible redness. After a while, however, it again becomes red hot, again sets fire to the gas, and thus the series of phenomena may be continually repeated (K. Kraut, *Ann. Ch. Pharm.* cxxxvi. 69).

Oxidation by Permanganates.—Ammonia heated with a large excess of permanganate and alkali is wholly converted into nitrate (Wanklyn a. Gamgee, *Chem. Soc. J.* [2] vi. 25).

Reaction of Ammonia with Sulphur, Selenium, Tellurium, and Phosphorus.—Flowers of sulphur washed and dried gradually absorb ammonia-gas; if heat be applied, nitrogen is set free, and ammonium sulphide is produced. Aqueous ammonia does not act on pure sulphur at temperatures below 75°, but towards 90° it assumes a yellow colour, in consequence of dissolving a small quantity of sulphur (Brunner. *Dingl. pol. J.* cl. 371). When aqueous ammonia of sp. gr. 0·885 is heated to 100° in a sealed tube for several days with a third of its weight of sulphur, the sulphur dissolves, forming a red-brown liquid which is not viscid and does not fume on exposure to the air. The solution consists mainly of ammonium polysulphides, and the residue left on evaporation is resolved by water into sulphur and ammonium hyposulphite (F. A. Flückiger, *J. Pharm.* [3] xlv. 453). *Selenium* heated with aqueous ammonia in sealed tubes forms a colourless solution of ammonium selenide, together with a small quantity of ammonium selenite. *Tellurium* yields an abundance of tellurite. Amorphous *phosphorus* is not acted on by ammonia; ordinary phosphorus gradually yields hydrogen phosphide and a compound of ammonia with an oxide of phosphorus; if alcoholic ammonia be used, the latter compound appears as a deep black metallic film adhering to the sides of the tube, and not decomposed by boiling sulphuric acid or potash-ley, whereby it is distinguished from the product obtained with aqueous ammonia (Flückiger, *loc. cit.*).

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[*] Stas prepared plumbiferous zinc free from carbon by fusing commercial zinc with 5 p. c. litharge. This alloy reacts with potassium nitrite and iron just like pure zinc, and readily eliminates hydrogen from dilute acids.

Respecting the action of ammonia on metals, see the several METALS; for its action on the chlorides of sulphur and phosphorus, see vol. iv. pp. 511, 515, 576, 606; v. 535.

Estimation of Ammonia in dilute solutions.—Nessler's reaction (i. 189) was applied by Hadow to the volumetric estimation of ammonia. By Wanklyn, Chapman, a. Smith this volumetric determination (which is especially adapted to very minute, and even microscopic quantities of ammonia) has been used in water-analysis, and in a general process for analysing nitrogenous organic substances (*Chem. Soc. J.* [2] vi. 161).

The 'Nessler liquor' is prepared by adding mercuric chloride to a hot concentrated solution of 50 grams potassium iodide till the precipitate no longer redissolves; then filtering; adding 150 grams of potassium hydrate in strong aqueous solution; diluting the liquid to a litre; adding another very small quantity of mercuric chloride; leaving the solution to settle; decanting; and preserving it in a well-closed vessel.

For the application of the 'Nessler liquor' to the quantitative estimation of ammonia, a very weak standard solution of ammonia is required. This is made by dissolving 0·3882 grams of ammonium sulphate (or the equivalent quantity of ammonium chloride) in one litre of water: it contains $\frac{1}{10}$ milligram of ammonia in one cubic centimetre. For general use, the standard may be advantageously diluted with water, so that one cubic centimetre shall contain $\frac{1}{100}$ milligram of ammonia.

The operation of measuring the quantity of ammonia in a given liquid is performed as follows: Two similar cylinders of colourless glass, each holding 100 c.c., and marked accurately at the 100 c.c. measure, are taken and put side by side. Into one is introduced 100 c.c. of the liquid to be tested, into the other the comparison-liquid, containing a measured volume of a standard solution of ammonia; 2 c.c. of 'Nessler liquid' is then to be dropped into each cylinder, and the depth of the resulting coloration observed. If the depth of colour of the comparison-fluid equals the depth of colour in the other glass, the quantity of standard ammonia which has been put into the comparison-fluid is the quantity actually present in the liquid to be tested. If the colour of the comparison-fluid is too high or too low, a fresh comparison-fluid must be made up, and this must be repeated until the right one is obtained.

Different metallic salts interfere with the action of the Nessler test. It is therefore advisable to distil off the ammonia, and apply the test to the distillate, which will contain nothing but ammonia-water.

The strength of ammonia to which the Nessler test is quantitatively applicable ranges from ·005 milligram to about 1 milligram per 100 c.c. It works best between 0·005 and 0·20 milligram per 100 c.c.

AMMONIUM ALLOYS. 1. *Ammonium Amalgam.*—Recent experiments on the substance known by this name lead to the conclusion that it is not a true amalgam — that is to say, a compound of mercury with a metallic radicle, NH^4—but merely a spongy mixture of metallic mercury with bubbles of nitrogen and hydrogen gases. Wetherill (*Sill. Am. J.* [2] xl. 160) finds that its formation may be prevented by certain so-called catalytic influences. When, for example, an ammoniacal salt is electrolysed with a negative pole formed of spongy platinum impregnated with mercury, no ammonium amalgam is formed, but a very brisk evolution of gases takes place. This doubtless arises from the circumstance that the mercury, being held within the pores of the platinum-sponge, is prevented from expanding so as to retain the gases. Landolt (*Zeitschr. f. Chem.* [2] v. 429) has shown that when the so-called ammonium amalgam is immersed in a solution of silver nitrate, ferric chloride, or cupric sulphate, no reduction of the metal or formation of an amalgam takes place, as is the case when an amalgam of potassium or sodium is used, but the ammonium amalgam is decomposed, as under ordinary circumstances, with evolution of nitrogen and hydrogen.

On the other hand, A. H. Gellatlin (*Zeitschr. f. Chem.* [2] v. 607) finds that when ammonium amalgam (prepared with sodium, but freed from excess of that metal) is placed in contact with small pieces of phosphorus, bubbles of phosphoretted hydrogen are evolved: hence he infers that the hydrogen evolved from the amalgam must be in the nascent state, and cannot therefore exist therein as free hydrogen.

But the most decisive experiments bearing on this question are those of Seeley (*Chem. News*, xxi. 265, June 10, 1870), from which it appears that when the amalgam is subjected to varying pressure, its volume changes like that of a gas. Into a tube 20 inches long and fitted with a plunger, mercury containing a little sodium was poured to half an inch in depth, and upon this was poured a strong solution of sal-ammoniac, occupying about two inches of the tube. The ammonium amalgam was completely formed in a few minutes, occupying several inches of the tube. On depressing the plunger, the volume of the amalgam progressively diminished till it closely approached the original volume of the mercury, which at the same time progressively gained fluidity and its usual mirror-like surface. On withdrawing the pressure, the compound resumed its original volume and dull frothy appearance. These results show that the ammonium, or rather its elements, NH^3 and H, exists in the amalgam, not as liquid, but as gas. The particles of the ammonia and hydrogen gases set free all over the surface of the mercury adhere to it, and as fresh particles of mercury are brought to the surface by the internal movements, they become enfilmed and carried inwards till the mixture becomes a homogeneous froth. Loew's so-called *hydrogenium amalgam*, obtained by agitating a dilute zinc amalgam with aqueous platinic chloride, is doubtless a mass of similar character.

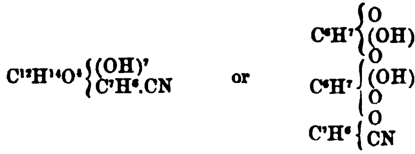
Pfeil a. Lippman (*Compt. rend.* lxii. 426) have endeavoured to prepare ammonium amalgams corresponding to the compound ammonias. A saturated solution of trimethylamine hydrochloride reacts with sodium amalgam just like a solution of sal-ammoniac, and the spongy amalgam produced quickly decomposes, with evolution of hydrogen, and formation of trimethylamine, which remains in solution. Saturated solutions of the hydrochlorides of aniline, conine, morphine, and quinine, also of rosaniline acetate, treated with sodium amalgam, give off large quantities of hydrogen, but do not form any product resembling ammonium amalgam. Hence also it appears that the physical properties of the ammonium amalgam are due to imprisoned gas-bubbles, and that those compound ammonias which are solid or liquid at ordinary temperatures do not form such amalgams. Pfeil a. Lippman also find that sodium amalgam does not act upon solid sal-ammoniac till a drop of water is added.

2. *Ammonium-bismuth* (?).—Gellatlin (*loc. cit.*) describes an alloy of ammonium and bismuth, prepared by pouring water in a fine rapid stream on an alloy of bismuth and sodium in contact with sal-ammoniac. The bismuth then swells up, becomes pasty and porous, and solidifies, giving off considerable quantities of hydrogen and ammonia. The compound immersed in a solution of copper quickly becomes covered with metallic copper, a property exhibited also by sodium-bismuth, but not by metallic bismuth. [The precipitation was perhaps due to sodium still present in the mass.] The ammonium-bismuth after drying in a vacuum over sulphuric acid gave off, when heated in a vacuum, 27 times its volume of gas consisting of hydrogen and nitrogen.

On Ammonium alloys, see also vol. v. pp. 328, 329.

AMPHITHALITE. A mineral from the Harrsjoeberg in Wermland, Sweden, occurring in hard, dense, milk-white veins or nodules, infusible, and not attacked by hydrochloric acid till after fusion with alkalis. Contains $(Ca; Mg)^2P^2O^7.7Al^2P^4O^{13} + 10aq.$, and therefore approximates in constitution to lazulite (Igelström, *J. pr. Chem.* c. 126; *Bull. Soc. Chim.* [2] viii. 41).

AMYGDALIN, $C^{20}H^{27}NO^{11}$, and **AMYGDALIC ACID,** $C^{20}H^{28}O^{12}$.—Schiff (*Zeitschr. f. Chem.* [2] v. 708) finds that seven of the hydrogen-atoms in amygdalin may be replaced by acid radicles, such as acetyl and benzoyl; hence he assigns to this compound a rational formula similar to that of arbutin, viz.,



$$C^{12}H^{14}O^4\left\{\begin{matrix}(OH)^7\\ C^7H^6.CN\end{matrix}\right. \quad \text{or} \quad \begin{matrix} C^6H^7\left\{\begin{matrix}O\\ (OH)^4\\ O\end{matrix}\right. \\ C^6H^7\left\{\begin{matrix}(OH)^3\\ O\end{matrix}\right. \\ C^7H^6\left\{\begin{matrix}O\\ CN\end{matrix}\right.\end{matrix}$$

Heptacetylamygdalin, $C^{12}H^{14}O^4\left\{\begin{matrix}(OC^2H^3O)^7\\ C^7H^6.CN\end{matrix}\right.$, is obtained by heating dehydrated amygdalin with excess of acetic anhydride to the boiling point of the latter. It crystallises from alcohol in long colourless anhydrous needles, having a silky lustre. At lower temperatures, acetylated amygdalins are formed, in which smaller numbers of hydrogen-atoms are replaced by acetyl.

Amygdalin cannot be supposed to contain the radicle benzoyl, C^7H^5O: for when treated with phosphorus pentachloride it yields only cyanogen chloride, benzylene chloride, and chlorinated derivatives of the latter, but no chloride of benzoyl; whereas the true benzoylated amygdalins, obtained by treating amygdalin with benzoyl chloride, reproduce the latter when subjected to the action of phosphorus pentachloride. Similar results are obtained by the action of bromine on amygdalin and benzoyl-amygdalin.

Amygdalin heated with *aniline* to 160°–180° is converted into amygdalanilide, $C^{12}H^{14}O^3(NC^7H^5)\left\{\begin{matrix}(OH)^7\\ C^7H^6.CN\end{matrix}\right.$, an uncrystallisable substance, decomposed even by solution in boiling water into amygdalin and aniline. The acetyl-amygdalins likewise yield anilides.

Amygdalin is not the amide of amygdalic acid, but is related to the latter in the same manner as methyl cyanide to acetic acid:

$$C^{12}H^{14}O^4\left\{\begin{matrix}(OH)^7\\ C^7H^6.CN\end{matrix}\right. \qquad\qquad C^{12}H^{14}O^4\left\{\begin{matrix}(OH)^7\\ C^7H^6.COOH\end{matrix}\right.$$

Amygdalin. Amygdalic acid.

Amygdalic acid treated with acetic anhydride is converted into a tetra- or a hepta-acetyl compound according as the reaction takes place at a lower or a higher temperature:

$$C^{12}H^{14}O^4\left\{\begin{matrix}(OC^2H^3O)^4\\ (OH)^3\\ C^7H^6.CO^2H\end{matrix}\right. \qquad\qquad C^{12}H^{14}O^4\left\{\begin{matrix}(OC^2H^3O)^7\\ C^7H^6.CO^2H\end{matrix}\right.$$

Tetracetamygdalic acid. Heptacetamygdalic acid.

Amygdalic acid is easily obtained in the form of a deliquescent crystalline mass. Its acetyl derivatives are insoluble in water and uncrystallisable, and are readily decomposed even by weak bases.

The formulæ of amygdalin and amygdalic acid above given afford a ready explanation of the formation of mandelic (formobenzoic) acid, $C^7H^6\left\{\begin{matrix}OH\\ CO^2H\end{matrix}\right.$, by heating amygdalin with hydrochloric acid (iii. 800).

AMYL. C^5H^{11}, and in the free state $C^{10}H^{22}$.—The isolated radicle is now more generally called diamyl. It is identical with decyl hydride, and when treated with chlorine yields chlorodiamyl or decyl chloride, $C^{10}H^{21}Cl$.

Diamyl is not attacked by nitric acid at ordinary temperatures, but at a gentle heat it is violently attacked by fuming nitric acid, and less energetically by acid of sp. gr. 1·4, yielding succinic acid, together with a liquid distillate, which appears to contain capronitrile, $C^{10}H^{19}N$, together with œnanthylic, valeric, and caproic acids (Schorlemmer, *Proc. Roy. Soc.* xvi. 372).

Wurtz obtained diamyl by the action of sodium on amyl iodide; and in like manner, amyl-ethyl, $C^5H^{11}.C^2H^5$, and amyl-butyl, $C^5H^{11}.C^4H^9$, by the action of sodium on a mixture of amyl iodide with ethyl iodide or butyl iodide (ii. 525; v. 732). Similarly, a mixture of the iodides of amyl and isopropyl treated with sodium (the mixture being cooled at first, and gently heated towards the end) yields amyl-isopropyl, $C^5H^{11}.CH(CH^3)^2$ or $C\left\{\begin{matrix}H\\ CH^3\\ CH^3\\ C^5H^{11}.\end{matrix}\right.$ Amyl-isopropyl boils at 109°–110°; its specific gravity is 0·6980 at 16·5°, and 0·6712 at 49°. It is probably identical with dibutyl, $C^4H^9.C^4H^9$, which, according to Kopp, boils at 109°, and has a sp. gr. of 0·7001 at 16·4°. (Respecting the constitutional formulæ of all these bodies, see HYDROCARBONS.)

Chlorine converts amyl-isopropyl into the chloride $C^8H^{17}Cl$, a colourless liquid which has an odour of oranges, like its isomeride, octyl chloride, a sp. gr. of 0·8834 at 10·5°, 0·8617 at 36°, and boils at 165°. With *iodine chloride* amyl-isopropyl forms a number of substitution-products, amongst which the chloride $C^8H^{17}Cl$ appears to be the most abundant. A solution of *chromic acid* attacks amyl-isopropyl very slowly, the only oxidation-products formed being carbonic and acetic acid (Schorlemmer, *Proc. Roy. Soc.* xvi. 37).

AMYL ALCOHOLS. $C^5H^{12}O$.—Of these alcohols there are eight possible varieties, viz. four primary, three secondary, and one tertiary.

Primary.

$$\mathrm{C}\left\{\begin{array}{l}\mathrm{CH^2CH^2CH^2CH^3}\\ \mathrm{H}\\ \mathrm{H}\\ \mathrm{OH}\end{array}\right. \qquad \mathrm{C}\left\{\begin{array}{l}\mathrm{CH^2CH(CH^3)^2}\\ \mathrm{H}\\ \mathrm{H}\\ \mathrm{OH}\end{array}\right. \qquad \mathrm{C}\left\{\begin{array}{l}\mathrm{CH}\begin{array}{l}\diagup\mathrm{CH^2CH^3}\\ \diagdown\mathrm{CH^3}\end{array}\\ \mathrm{H}\\ \mathrm{H}\\ \mathrm{OH}\end{array}\right. \qquad \mathrm{C}\left\{\begin{array}{l}\mathrm{C(CH^3)^3}\\ \mathrm{H}\\ \mathrm{H}\\ \mathrm{OH}\end{array}\right.$$

Secondary.

$$\mathrm{C}\left\{\begin{array}{l}\mathrm{CH^2CH^2CH^3}\\ \mathrm{CH^3}\\ \mathrm{H}\\ \mathrm{OH}\end{array}\right. \qquad \mathrm{C}\left\{\begin{array}{l}\mathrm{CH(CH^3)^2}\\ \mathrm{CH^3}\\ \mathrm{H}\\ \mathrm{OH}\end{array}\right. \qquad \mathrm{C}\left\{\begin{array}{l}\mathrm{CH^2CH^3}\\ \mathrm{CH^2CH^3}\\ \mathrm{H}\\ \mathrm{OH.}\end{array}\right.$$

Tertiary.

$$\mathrm{C}\left\{\begin{array}{l}\mathrm{CH^2CH^3}\\ \mathrm{CH^3}\\ \mathrm{CH^3}\\ \mathrm{OH.}\end{array}\right.$$

Primary. *Normal Amyl alcohol* or *Butyl carbinol*, $\mathrm{C}\left\{\begin{array}{l}\mathrm{CH^2CH^2CH^2CH^3}\\ \mathrm{H^2}\\ \mathrm{OH,}\end{array}\right.$ has been quite recently obtained by Lieben a. Rossi (*Compt. rend.* lxxi. 370) by a synthetical process from normal butyl alcohol, $\mathrm{C}\left\{\begin{array}{l}\mathrm{CH^2CH^2CH^3}\\ \mathrm{H^2}\\ \mathrm{OH}\end{array}\right.$ (p. 63), which had been prepared from normal butyric acid. The butyl alcohol was transformed into the cyanide, and from the latter, normal valeric acid, boiling at 185°, was prepared. The calcium salt of this acid was mixed with calcium formate and distilled, and the valeral thus obtained was hydrogenated with sodium amalgam, and thereby converted into the alcohol. The amyl alcohol thus produced boils at 137° under a pressure of 744 mm. (ordinary amyl alcohol boils at about 132°); the chloride, bromide, iodide, and acetate obtained from it likewise boil at higher temperatures than the corresponding ordinary amyl-compounds. In most respects, however, normal amylic alcohol resembles the alcohol from fusel-oil. By oxidation it yields a valeric acid, which is the normal acid, $\mathrm{C}\left\{\begin{array}{l}\mathrm{CH^2CH^2CH^2CH^3}\\ \mathrm{O}\\ \mathrm{OH}\end{array}\right.$, boiling at 185° and smelling somewhat like butyric acid.

Isobutyl Carbinol. $\mathrm{C}\left\{\begin{array}{l}\mathrm{CH^2CH(CH^3)^2}\\ \mathrm{H^2}\\ \mathrm{OH}\end{array}\right.$.—This, as shown by Erlenmeyer, is the constitution of the ordinary amylic alcohol of fermentation, which is therefore the true homologue of Wurtz's butylic alcohol, itself likewise a product of fermentation. The latter yields by oxidation with chromic acid, not normal butyric, but isobutyric acid, $\mathrm{CH(CH^3)^2.CO^2H}$. (See Butyl Alcohols.) Now the butyl cyanide, $\mathrm{CH^2CH(CH^3)^2.CN}$, prepared from this fermentation butyl alcohol, is converted by boiling with alcoholic potash into a valeric acid, $\mathrm{CH^2CH(CH^3)^2.COOH}$, identical in every respect with ordinary valeric acid, obtained from valerian root, or by oxidation of ordinary amyl alcohol. This alcohol must, therefore, contain the same radicle as the valeric acid prepared from butyl cyanide, that is to say, it must consist of isobutyl carbinol (Erlenmeyer, *Ann. Ch. Pharm. Suppl.* v. 337; *Jahresb.* 1867, p. 580).

But ordinary fusel-oil, as shown some years ago by Pasteur (i. 205), contains two isomeric amyl alcohols, one active, the other inactive, to polarised light. Both of these are primary alcohols, yielding valeric acid by oxidation, the acid thus obtained being, however, optically-active or inactive, according as it is obtained from the active or inactive alcohol. The question then arises, Are these two alcohols merely physically isomeric, or are they metameric, the one containing normal butyl, the other isobutyl? This question has not yet been answered with certainty; but from the recent experiments of Pedler (*Chem. Soc. J.* [2] vi. 74) it appears that the two alcohols exhibit the closest resemblance to one another in all their physical properties, excepting their relation to polarised light. They have the same smell and taste, and their boiling points differ by only one degree, the active alcohol boiling at 128°, the inactive alcohol at 129° (according to other authorities the boiling point of amylic alcohol is 132°). The active alcohol rotates a yellow ray of polarised light 17° to the left in a tube 50 centimetres long. The close resemblance of the two alcohols in all other physical properties points rather to physical than to chemical isomerism, being probably indeed the kind of isomerism which exists between the several varieties of turpentine oil (which are in like manner distinguished from one another chiefly by their behaviour to polarised light), and being due to differences of arrangements in the molecules of the body, rather than to differences of constitution in the molecules themselves.

In their behaviour with oxidising agents, however, the two amylic alcohols exhibit a certain amount of difference. The inactive alcohol when heated with potassium dichromate and dilute sulphuric acid yields nothing but ordinary inactive valeric acid, whereas the active (lævogyrate) alcohol heated with the same oxidising mixture is converted into acetic and carbonic acids; in the cold, however, it is oxidised to *dextrogyrate* valeric acid, producing a rotation of 43° in a tube 50 centimetres long.

From these results it may be concluded that inactive amyl alcohol certainly consists of isobutyl carbinol, $CH^2CH(CH^3)^2.CH^2OH$; but whether the active alcohol consists of the third or fourth modification above enumerated, or is merely a physical modification of the inactive alcohol, is a question requiring further investigation; but, as already observed, the latter supposition appears to be the more probable of the two.

Chapman a. Smith (*Proc. Roy. Soc.* xvii. 308) find that the separation of the active and inactive amyl alcohols may be effected much more easily than by Pasteur's method (i. 203), by dissolving soda, potash, or chloride of calcium in crude amyl alcohol at the boiling heat, and distilling the saturated solution, the non-rotating alcohol being then to a great extent retained, while the rotating alcohol distils off. Almost any salt easily soluble in amyl alcohol might be used for the purpose, but the substance which answers best is caustic soda. The amyl alcohol is boiled with caustic soda, and the hot solution is decanted into a flask and distilled from an oil-bath, the temperature being kept below 200°. The alcohol distils off quickly at first, afterwards more slowly, and, finally, the contents of the flask solidify, after which it becomes very difficult to distil off any more amyl alcohol. On now adding water and again distilling, amyl alcohol comes over of about half the rotating power of the alcohol employed. By a sufficient number of repetitions of this process it is possible to effect a separation of the alcohols, and very easy to obtain considerable quantities of the non-rotating alcohol quite pure.

Chapman has subsequently found that the rotating alcohol is actually converted into the non-rotating alcohol by repeated distillation over caustic soda.

Schorlemmer (*Proc. Roy. Soc.* xv. 131) has shown that the amyl-compounds obtained from fusel-oil and from American petroleum agree so nearly in specific gravity and boiling point that they may be regarded as identical. The results are given in the following table:

	From fusel-oil		From petroleum	
	B. P.	Sp. gr.	B. P.	Sp. gr.
Amyl hydride, C^5H^{12} . . .	—	—	34°	0·6263 at 17°
Amyl chloride, $C^5H^{11}Cl$ . . .	101°	0·8750 at 20°	101°	0.8777 at 20°
Amyl acetate, $C^5H^{11}.C^2H^3O^2$ . .	140°	0·8733 at 15°	140°	0·8752 at 15°
Amyl alcohol, $C^5H^{12}O$ . . .	132°	0·8148 at 14°	132°	0·8199 at 14°

Lastly, Wurtz has shown that valeral, $C^4H^9.COH$, treated for fifteen days with sodium amalgam and water, takes up 2 at. hydrogen and is converted into a primary amyl alcohol (*Ann. Ch. Pharm.* cxxxiv. 301).

The following statements all relate to the amylic alcohol of fermentation:—

Solubility.—1 pt. of amyl alcohol dissolves in 3·9 pts. *water* at 16·5°, forming a liquid of sp. gr. 0·998. On the other hand, 1 pt. of water mixes with 11·625 pts. amyl alcohol at 16·5°, forming a clear liquid of sp. gr. 0·8350 (Wittstein, *Jahresb.* 1862, p. 408). Amyl alcohol dissolves in all proportions of *acetic acid* diluted with an equal quantity of water, and may be thereby separated from neutral amylic ethers which are not soluble in acetic acid (Berthelot a. St. Gilles, *Jahresb.* 1862, p. 409). It dissolves 3½ vol. *acetylene* at 18° (Berthelot, *Ann. Ch. Phys.* [4] ix. 425).

Reactions.—1. Vapour of amyl alcohol is decomposed by the passage of *electric sparks* in a barometric vacuum, with formation of acetylene (De Wilde, *Bull. Soc. Chim.* [2] vi. 267).—2. The vapour passed through a tube heated to low redness is resolved into a mixture of gases, chiefly propylene (Reynolds, i. 203), together with ethylene, butylene, liquid hydrocarbons (Wurtz, *Ann. Ch. Phys.* [3] li. 84), and a small quantity of acetylene (Caventou, *Bull. Soc. Chim.* [2] v. 162). If the heat is very strong, the product consists almost wholly of marsh gas (Reynolds).—3. Amyl alcohol exposed to the *air*, either in direct sunshine or in diffused daylight, is gradually oxidised, yielding hydrogen dioxide and an acid, probably valeric acid (Schönbein, *J. pr. Chem.* xcviii. 261). When shaken up with *ozonised air*, it is oxidised to valeraldehyde and valeric acid (Gorup-Besanez, *Ann. Ch. Pharm.* cx. 103).

4. When *nitric acid* of sp. gr. 1·5 is covered with a nearly equal volume of amyl alcohol, the two being separated by a layer of water, and the whole left to itself for a month, amyl valerate is formed, together with oxalic acid and a yellow colouring matter (Claus, *J. pr. Chem.* cii. 384). Amyl alcohol heated to 90° absorbs *nitrogen tetroxide*, forming amyl nitrite and nitric acid:

$$C^5H^{12}O + N^2O^4 = C^5H^{11}NO^2 + HNO^3;$$

and the nitric acid thus formed converts part of the amyl alcohol into amyl nitrate, and by oxidation into hydrogen valerate (valeric acid) and amyl valerate. Vapour of *nitrous acid* (from starch and nitric acid) passed into amyl alcohol forms amyl nitrite and ammonium nitrate, which separate in crystals (N. Bunge, *Zeitschr. f. Chem.* [2] ii. 82).

5. Solutions containing 3 to 8 p. c. *potassium dichromate* and a sufficient quantity of *sulphuric acid* oxidise amyl alcohol to valeric acid and amyl valerate; but the more volatile portion of the distillate obtained by fractional distillation from a sample of commercial amyl alcohol yielded, when thus treated, valeric, butyric, and carbonic acids, probably owing to the presence of a secondary amyl alcohol in the commercial product (Chapman a. Thorp, *Chem. Soc. J.* [2] iv. 477).

6. When amyl alcohol is boiled with *sulphur*, a small quantity of hydrogen sulphide is evolved; sulphuretted products are obtained in larger quantity by passing the vapour of the alcohol into boiling sulphur (Brian, *Jahresb.* 1863, p. 467).

7. When *chlorine gas* is passed into amyl alcohol, the liquid becomes hot, giving off hydrochloric acid and amyl chloride; if the action be prolonged (with a few ounces of the alcohol it goes on for eight or ten days), the ultimate product is the compound $C^5H^7Cl^5$, and intermediate products are formed agreeing approximately with the formulæ $C^5H^9ClO^2$ and $C^5H^8Cl^2O^2$; the latter when decomposed with alcoholic potash yields valeric acid. The compound $C^5H^7Cl^5$ treated with alcoholic potash yields a liquid, $C^5H^6Cl^4$, boiling above 200° (Barth, *Ann. Ch. Pharm.* cxix. 216).

8. Amyl alcohol distilled with water and *chloride of lime* yields, besides chloroform, a liquid which boils at 70°, has a density of 0·88 at 0°, and exhibits the composition of butyl chloride, C^4H^9Cl (F. Gerhard, *Ann. Ch. Pharm.* cxxii. 363).

9. With *phosphorus trichloride*, amyl alcohol yields amyl chloride and amyl phosphorous chloride, $PC^5H^{11}OCl^2$ (Menschutkin, *Ann. Ch. Pharm.* cxxxix. 343). (For the action of PCl^5, see i. 201.) *Phosphorus cyanide* acts strongly on amyl alcohol, forming amyl phosphite and hydrocyanic acid (Wehrhane a. Hübner, *Ann. Ch. Pharm.* cxxxii. 283).

10. With *chlorine disulphide*, S^2Cl^2, amyl alcohol mixes to a yellow liquid which evolves hydrochloric acid and sulphurous oxide, and when heated deposits sulphur, gives off amyl chloride, then becomes carbonised and gives off stinking sulphuretted products. With excess of amyl alcohol, the products are chloride, sulphite, and sulphydrate of amyl (Carius a. Fries, *Ann. Ch. Pharm.* cix. 1):

$$\underset{\substack{\text{Amyl}\\\text{alcohol.}}}{C^5H^{12}O} + \underset{\substack{\text{Chlorine}\\\text{disulphide.}}}{S^2Cl^2} = \underset{\substack{\text{Amyl}\\\text{sulphydrate.}}}{C^5H^{12}S} + \underset{\substack{\text{Thionyl}\\\text{chloride.}}}{SOCl^2}$$

and

$$\underset{\substack{\text{Amyl}\\\text{sulphydrate.}}}{4C^5H^{12}S} + \underset{\substack{\text{Thionyl}\\\text{chloride.}}}{3SOCl^2} = S^6 + 4HCl + \underset{\substack{\text{Amyl}\\\text{sulphite.}}}{(C^5H^{11})^2SO^3} + \underset{\substack{\text{Amyl}\\\text{chloride.}}}{2C^5H^{11}Cl}$$

With *sulphur dichloride*, SCl^2 (a mixture of chlorine disulphide and sulphur tetrachloride, v. 535), amyl alcohol forms hydrochloric acid, sulphurous oxide, amyl chloride, and chlorine disulphide (Carius a. Fries):

$$2C^5H^{12}O + SCl^4 = 2HCl + SO^2 + 2C^5H^{11}Cl.$$

With *thionyl chloride*, amyl alcohol forms hydrochloric acid and amyl sulphite (Carius, *Ann. Ch. Pharm.* cxi. 98).

11. Amyl alcohol distilled with *zinc chloride* gives off, in addition to amylene and amyl hydride, other hydrocarbons homologous with these, varying in boiling point from below 50° to above 400°, and leaves an undistillable carbonaceous residue (Wurtz). If the distillation be interrupted at 140°–160°, the residue contains triamylene and tetramylene (Bauer, *Zeitschr. Ch. Pharm.* 1861, p. 645). On distilling amyl alcohol for 24 hours with 1½ pts. of recently fused and pulverised zinc chloride, separating the portion of the oily distillate which boils below 50° and contains amylene and amyl hydride, treating the portions of higher boiling point once more

with zinc chloride, and further with sodium, to remove unaltered amyl alcohol, a liquid is obtained which yields by fractional distillation, (*a*) between 60° and 70°, hexylene and hexyl hydride; (*b*) between 80° and 85°, heptylene and heptyl hydride; (*c*) between 120° and 130°, octylene and octyl hydride; (*d*) between 135° and 150° nonylene and nonylhydride; (*e*) diamylene and diamylhydride; and, lastly, thick oily hydrocarbons boiling above 400°. The greater number of these hydrocarbons are however formed, not from the amyl alcohol itself, but from small quantities of other alcohols mixed with it (Wurtz, *Bull. Soc. Chim.* 1863, p. 461; *Ann. Ch. Pharm.* cxxviii. 316).

12. Amyl alcohol boiled with solution of *platinic chloride* yields amylene platinoso-chloride, $2(C^5H^{10}.HCl).Pt{\cdot}Cl^4 + 2aq.$, together with valeraldehyde and chlorinated products (Birnbaum, *Ann. Ch. Pharm.* cxlv. 67).

13. When 10 pts. amyl alcohol are added to 2 pts. *mercury* dissolved in 12 pts. *nitric acid*, a brisk reaction takes place and oxalic acid is formed, but no product analogous to fulminating mercury; the cooled liquid deposits crystals of a double salt of mercurous oxalate and mercuric nitrate (v. Gilm, *Jahresb.* 1858, p. 402).

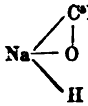
14. When amyl alcohol is heated with *ethyl acetate* (α), *iodide* (β), or *oxalate* (γ), there is formed, by double decomposition between the amyl alcohol and a portion of these ethers: α. Amyl acetate and ethyl alcohol; β. Amyl iodide, ethyl alcohol, and ethyl-amyl oxide; γ. Amyl oxalate and ethyl-amyl oxalate (Friedel a. Crafts, *Ann. Ch. Pharm.* cxxx. 198; cxxxi. 55).

Sodium Amylate or ***Amylene-sodium Hydrate***. $C^5H^{11}NaO$.—The crystalline body produced by the action of sodium on amyl alcohol (i. 205) is commonly regarded as sodium amylate, $\left.\begin{matrix}C^5H^{11}\\ Na\end{matrix}\right\}O$, derived from amyl alcohol, $\left.\begin{matrix}C^5H^{11}\\ H\end{matrix}\right\}O$, by substitution of sodium for the typic hydrogen. But from recent investigations by Wanklyn (*Phil. Mag.* [4] xxxvii. 117, 175), it appears that this crystalline body, when dried at 100°, has the composition $C^5H^{11}NaO.3C^5H^{12}O$, that is, 1 mol. sodium amylate with 3 mol. amyl alcohol, and that when heated to about 200° it gives off the whole of the amylic alcohol, leaving pure or absolute sodium amylate, $C^5H^{11}NaO$. This same compound may be obtained by the action of amyl alcohol on sodium ethylate:

$$C^2H^5NaO + C^5H^{11}OH = C^2H^5(OH) + C^5H^{11}NaO.$$

Moreover, from numerous considerations relating to the constitution and chemical functions of sodium compounds, Wanklyn infers that sodium is not univalent, as commonly supposed, but trivalent, sodium hydrate consisting of $Na'''\left\{\begin{matrix}H\\ O''\end{matrix}\right.$, sodium acetate of $Na'''\left\{\begin{matrix}C^2H^3O\\ O''\end{matrix}\right.$, &c. (See SODIUM.)

In accordance with this view, sodium amylate, $C^5H^{11}NaO$, must be regarded as **amylene-sodium hydrate**, and represented by the formula



or

$$Na'''\left\{\begin{array}{l}C^5H^{10}\\ \ |\\ O\\ H\end{array}\right.$$

Amylene-sodium hydrate treated with *ethyl valerate* is converted into amylene-sodium valerate and ethyl alcohol:

$$Na\left\{\begin{array}{l}C^5H^{10}\\ \ |\\ O\\ H\end{array}\right. + \left.\begin{matrix}C^2H^5\\ C^5H^9O\end{matrix}\right\}O = \left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\}O + Na'''\left\{\begin{array}{l}C^5H^{10}\\ \ |\\ O\\ C^5H^9O\end{array}\right.$$

Amylene sodium acetate, $\overbrace{C^5H^{10}\!-\!O\ C^2H^3O}^{Na'''}$, is obtained in like manner. This salt, or ether, is isomeric with sodium œnanthylate, $C^7H^{13}NaO^2$, and the valerate above mentioned with sodium rutate or caprate, $C^{10}H^{19}NaO^2$. These ethers react with *water* in such a manner as to yield an ordinary salt of the acid whose radicle they contain, together with amyl alcohol; e.g.,

$$\underset{\text{Amylene-sodium acetate.}}{Na\left\{\begin{array}{l}C^5H^{10}\\ \ |\\ O\\ C^2H^3O\end{array}\right.} + H^2O = \underset{\text{Amyl alcohol.}}{C^5H^{12}O} + \underset{\text{Sodium acetate.}}{Na\left\{\begin{matrix}O\\ C^2H^3O\end{matrix}\right.}$$

All these reactions have been more closely studied with the ethylene sodium compounds (*q.v.*).

Sodium amylate treated with *chloroform* yields sodium chloride and a triamylic ether, analogous in constitution to the tri-alcoholic glycerides (Williamson a. Kay, *Chem. Soc. Qu. J.* vii. 224):

$$CHCl^3 + 3C^5H^{11}NaO = 3NaCl + \left.\begin{matrix}(CH)'''\\(C^5H^{11})^3\end{matrix}\right\}O^3.$$

Thallium Amylate, $C^5H^{11}TlO$, described amongst thallium compounds (v. 757), may be regarded in like manner as $Tl'''\left\{\begin{matrix}C^5H^{10}\\|\\O\\H\end{matrix}\right.$.

Compound of Amyl Alcohol with Stannic Chloride.—When anhydrous stannic chloride is poured, with careful exclusion of air, into pure amyl alcohol cooled to between −10° and −17°, a nearly colourless mass is formed, consisting of the amyl alcoholate of stannic chloride, $SnCl^4.2C^5H^{12}O$. This compound forms colourless tabular crystals, which deliquesce rapidly on exposure to the air, and are instantly decomposed by water into stannous chloride, hydrochloric acid, and amyl alcohol. It dissolves in benzol, chloroform, and carbon bisulphide, and may be recrystallised from these solutions over sulphuric acid in a vacuum, though not without partial decomposition. Heated to 100° in a sealed tube and then distilled, it yields, together with a yellow liquid, white feathery crystals of the hydrate of stannic chloride, $SnCl^4.3H^2O$, described by Casselmann (v. 808). The yellow liquid, after washing with dilute alkali, yields by fractional distillation, from 40° to 100°, moderately pure amylene; from 100° to 170°, chiefly amylene chloride, $C^5H^{12}Cl^2$; and from 170° to 400°, polymerides of amylene, mixed with a small quantity of chlorinated amylenes. The decomposition of the amyl-alcoholate of stannic chloride by heat may therefore be represented essentially by the following equation:

$$2(SnCl^4.2C^5H^{12}O) = SnCl^4.3H^2O + SnCl^2.H^2O + 3C^5H^{10} + C^5H^{10}Cl^2$$

(Bauer a. Klein, *Zeitschr. f. Chem.* [2] iv. 379).

Primary Amylic Haloïd Ethers.

Amyl Bromide, $C^5H^{11}Br$, is best prepared by saturating amyl alcohol with gaseous hydrobromic acid, mixing the saturated solution with an equal volume of the aqueous acid of sp. gr. about 1·5, and digesting slowly at the heat of the water-bath, either in a flask with a vertical condensing tube, or in a closed vessel. The amyl bromide which rises to the surface must be decanted, washed with water, and distilled from under a solution of sodium carbonate. The distillate consists of water and the bromide, which has then to be dried over calcium chloride and fractionally distilled. If the amyl alcohol was pure, the bromide boils quite constantly; if not, it fractionates very easily. The pure bromide boils at 121° (at 118·7° according to Mendelejef, *Jahresb.* 1860, p. 7), and has a sp. gr. of 1·217 at 16° (1·058 at 0°, Pierre; 1·2059 at 15·7°, Mendelejef). It is very strongly attacked by sodium at temperatures near its boiling point (Chapman a. Smith, *Chem. Soc. J.* [2] vii. 198).

Amyl Chloride, $C^5H^{11}Cl$, is produced by treating 90 pts. amyl alcohol with 200 pts. brown chloride of sulphur (a mixture of S^2Cl^2 with SCl^4, v. 535). The action is very violent at first, hydrochloric acid and sulphurous oxide being given off, for the complete removal of which the mixture must be heated to 101°. At 110° amyl chloride distils over, amounting, after washing with weak soda-ley, drying, and rectifying, to 100 pts. (Carius a. Fries, *Ann. Ch. Pharm.* cix. 1).

Boiling point 101·75° under pressure of 752·4 mm. (Pierre, *Jahresb.* 1851, p. 51); 98° (Rossi, *Ann. Ch. Pharm.* cxxxiii. 176); corr. 100·9°, under pressure of 745·6 mm. (Kopp; Carius a. Fries). Sp. gr. 0·8625 at 25·1°; 0·8859 at 0° (Kopp, *Jahresb.* 1855, p. 35); 0·8958 at 0° (Pierre); 0·8744 at 15·7 (Mendelejef. *ibid.* 1860, p. 7).

Amyl chloride is very slowly decomposed by *water* at 100° into hydrochloric acid and amyl alcohol (Butlerow, *Ann. Ch. Pharm.* cxliv. 34). *Chlorine* passed through it converts it into carbon trichloride, C^2Cl^6 (Gerhard, *ibid.* cxxii. 363). With strong *sulphuric acid* it yields hydrochloric and amyl-sulphuric acids (Oppenheim, *J. pr. Chem.* cii. 339). With *alcoholic potash* it forms ethyl-amyl oxide (Reboul a. Truchot, *Compt. rend.* lxiv. 1243). Heated with *sodium acetate* or *benzoate*, it forms amyl acetate or benzoate, together with a small quantity of amylene (Berthelot, *Ann. Ch. Pharm.* cxxvii. 69).

When chlorine is passed in diffused daylight and at ordinary temperatures through amyl hydride from American petroleum, a mixture of chlorinated products is formed, from which by fractional distillation an amyl chloride may be separated boiling at 98°–103°. This chloride, treated with sulphydrate and monosulphide of potassium, and with alcoholic ammonia, yields amyl-compounds; but with alcoholic potash it yields a large quantity of amylene (Pelouze a. Cahours, *Ann. Ch. Phys.* [4] i. 13): from this it appears probable that a secondary amyl chloride is formed simultaneously with the primary chloride.

Amyl Iodide. $C^5H^{11}I$.—Produced, together with ethyl alcohol, by heating amyl alcohol with ethyl iodide; the decomposition, however, is only partial; and, on the other hand, ethyl alcohol and amyl iodide react partially, producing amyl alcohol and ethyl iodide (Friedel a. Crafts, *Ann. Ch. Pharm.* cxxx. 198).

According to Grimm (*J. pr. Chem.* lxii. 385), the directions usually given for the preparation of this compound prescribe too large a proportion of amyl alcohol. Grimm uses 5 parts iodine to 4 parts amyl alcohol. The alcohol mixed with 4 to 5 per cent. water is saturated with iodine; the decanted solution is heated to 50° and decolorised with phosphorus, then decanted from the phosphorus, and poured back on the undissolved iodine, again decolorised with phosphorus, and so on, till the whole of the iodine is used up. The fuming liquid is distilled after 24 hours, the distillate shaken up with water and iodine, as long as the colour of the iodine is thereby destroyed, then washed, dried, and rectified, the pure amyl iodide passing over at 149°.

Sp. gr.	Boiling point (corr.)	Observers
1·5087 at 15·8° (referred to water at 4°)	. . . . . .	Mendelejef (*Compt. rend.* l. 52).
1·4387 at 22·3°		
1·4678 at 0°	. . 147·2° to 147·7° (bar. 740·2° mm.)	Kopp (*Jahresb.* 1853, p. 37).
1·4936 at 20°	. . . . 149° . . .	Grimm.

Reactions.—Amyl iodide is slowly oxidised to valeric acid by a 5 per cent. aqueous solution of *potassium dichromate* and *sulphuric* acid (Chapman a. Thorp, *Chem. Soc. J.* [2] iv. 477). Heated with moist *silver oxide* to 100°, it forms silver iodide and amyl alcohol, together with small quantities of amyl oxide and amylene (Wurtz, *Ann. Ch. Phys.* [3] xlvi. 223).

When 2 at. *silver cyanide* and 1 at. amyl iodide are heated together to the boiling point of the latter, a very violent action takes place, equal volumes of amylene and hydrocyanic acid being given off, and a black mass remaining, which consists of silver iodide and a compound of silver cyanide with amyl cyanide, and when further heated gives off hydrocyanic acid, amylene, and amyl cyanide (Hofmann, *Zeitschr. f. Chem.* [2] iii. 665).

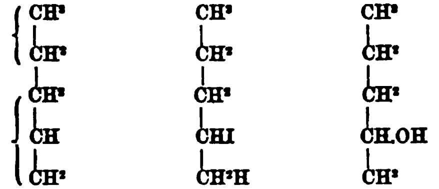
For the reactions of amyl iodide with sodium, see i. 202; with sodium ethylate and methylate, i. 205; with zinc, iv. 219; with sodium stannide, v. 835; with sodium plumbide, iii. 560; with sodium amalgam in presence of acetic ether, iii. 924; with cacodyl, i. 411; with ethyl oxalate, amyl oxalate, &c., and zinc, iv. 278.

Secondary Amyl Alcohols. The secondary alcohol $C^4H^{10}.CHOH$ or $C^5H^{10}.H^2O$ admits of the three following modifications:

$$\begin{array}{ccc}
\mathrm{C}\left\{\begin{matrix}\mathrm{CH^2CH^2CH^3}\\ \mathrm{CH^3}\\ \mathrm{H}\\ \mathrm{OH}\end{matrix}\right. & \mathrm{C}\left\{\begin{matrix}\mathrm{CH(CH^3)^2}\\ \mathrm{CH^3}\\ \mathrm{H}\\ \mathrm{OH}\end{matrix}\right. & \mathrm{C}\left\{\begin{matrix}\mathrm{CH^2CH^3}\\ \mathrm{CH^2CH^3}\\ \mathrm{H}\\ \mathrm{OH}\end{matrix}\right. \\
\text{Propyl-methyl carbinol.} & \text{Isopropyl-methyl carbinol.} & \text{Diethyl carbinol.}
\end{array}$$

The first two of these are actually known.

PROPYL-METHYL CARBINOL is produced: 1. By combining ethyl-allyl, $C^2H^5.C^3H^5$, with hydriodic acid, and distilling the resulting secondary amyl iodide, $C^5H^{10}.HI$, with silver oxide and water, or, better, by converting the iodide into the corresponding acetate, $C^5H^{10}.H.C^2H^3O^2$, by means of silver-acetate, and distilling the purified acetate at 120° with very strong potash-ley and sticks of potash. The passage from the ethyl-allyl through the iodide to the alcohol may be represented by the following structural formulæ:—



$$\begin{array}{ccc}
\left\{\begin{matrix}\mathrm{CH^3}\\ |\\ \mathrm{CH^2}\end{matrix}\right. & \begin{matrix}\mathrm{CH^3}\\ |\\ \mathrm{CH^2}\end{matrix} & \begin{matrix}\mathrm{CH^3}\\ |\\ \mathrm{CH^2}\end{matrix} \\
| & | & | \\
\left\{\begin{matrix}\mathrm{CH^2}\\ |\\ \mathrm{CH}\\ |\\ \mathrm{CH^2}\end{matrix}\right. & \begin{matrix}\mathrm{CH^2}\\ |\\ \mathrm{CHI}\\ |\\ \mathrm{CH^2H}\end{matrix} & \begin{matrix}\mathrm{CH^2}\\ |\\ \mathrm{CH.OH}\\ |\\ \mathrm{CH^3}\end{matrix} \\
\text{Ethyl-allyl.} & \text{Secondary amyl iodide.} & \text{Secondary amyl alcohol.}
\end{array}$$

(Wurtz, *Zeitschr. f. Chem.* [2] iv. 490).

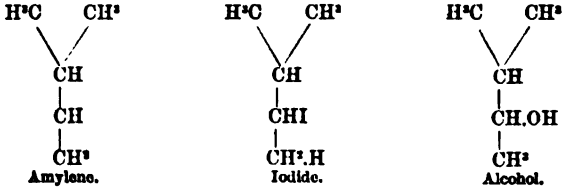
2. By decomposing propyl-methyl ketone (obtained by distilling a mixture of calcium butyrate and acetate) with sodium amalgam and water (Friedel, *ibid.* v. 486).

$$C\left\{\begin{array}{l}C^3H^7\\CH^3\\O''\end{array}\right. \quad + \quad H^2 \quad = \quad C\left\{\begin{array}{l}C^3H^7\\CH^3\\H\\OH.\end{array}\right.$$

Propyl-methyl carbinol has an odour like that of ordinary amyl alcohol, but less pungent; sp. gr. = 0·8249 – 0·8260 at 0°; boiling point 120° under a pressure of 759 mm. (Wurtz), 120° – 123° (Friedel); insoluble in water; oxidised by *potassium permanganate*, yielding a neutral liquid which unites with acid sodium sulphite, and when separated from that combination boils at 103°, and exhibits nearly the composition of propyl-methyl ketone, $C^5H^{10}O$. Acetic and propionic acids are likewise produced in the oxidation. The alcohol treated with *chromic acid* does not yield carbon dioxide (Wurtz). Treated with *iodine* and *phosphorus*, it yields the corresponding iodide, $C^5H^{10}.HI$, which when decomposed by silver acetate, yields amylene, together with the corresponding amylic acetate, $C^5H^{10}.H.C^2H^3O^2$.

ISOPROPYL-METHYL CARBINOL, $\left.\begin{array}{r}CH(CH^3)^2\\CH^3\end{array}\right\}CHOH$, or **AMYLENE MONOHYDRATE,** $C^5H^{10}.H^2O$, discovered by Wurtz (*Ann. Ch. Phys.* [4] iii. 137), is produced by combining amylene (from ordinary amyl alcohol) with hydriodic acid, adding the resulting hydriodide by small quantities at a time to an equivalent quantity of moist silver oxide in a vessel surrounded with ice, then leaving the mixture to itself for a while, and distilling. The alcohol then passes over with the water; afterwards the boiling point rises to about 160°, and above that temperature the corresponding ether, $C^5H^{10}.H(OC^5H^{11})$, passes over. Ordinary amylene hydriodide is decomposed by silver oxide much more easily than the isomeric compound ethyl-allyl hydriodide.

The passage from amylene through the iodide to the alcohol is represented by the following formulæ:



Amylene. Iodide. Alcohol.

Isopropyl-methyl carbinol is a light, colourless, very mobile liquid, boiling at 105° (bar. 768 mm.) (Wurtz), at 108° (Kolbe), i.e. from 12° to 15° lower than methyl-propyl carbinol. Heated for some hours to 200°, it splits up into amylene and water. It absorbs *hydriodic acid* rapidly and with rise of temperature, forming water and amylene hydriodide; with *bromine* it forms chiefly amylene dibromide; with *chlorine*, amylene dichloride and hydrochloride. When shaken up with *sulphuric acid*, it becomes hot and yellow, and is converted, not into amylsulphuric acid, like the primary alcohol, but into amylene and hydrocarbons polymeric therewith. With *sodium* it forms sodium amylenate, $C^5H^{10}.Na(OH)$ [probably identical with Wanklyn's hydrate of amylene-sodium, p. 109], which when treated with amylene hydriodide reproduces the secondary alcohol and amylene:

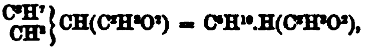
$$C^5H^{10}\left\{\begin{array}{l}Na\\OH\end{array}\right. + C^5H^{10}\left\{\begin{array}{l}H\\I\end{array}\right. = NaI + C^5H^{10} + C^5H^{10}\left\{\begin{array}{l}H\\OH.\end{array}\right.$$

When oxidised by *potassium dichromate* and *sulphuric acid*, it gives off carbon dioxide, volatile acids, chiefly acetic acid, a mixture of ketones, &c.; with *potassium permanganate*, the same products (Wurtz). According to Kolbe (*Ann. Ch. Pharm.* cxxxii. 102; *Jahresb.* 1864, p. 502), the oxidation is of a more definite character. On gradually pouring the alcohol into a hot aqueous solution of 2 pts. potassium dichromate mixed with 3 pts. sulphuric acid, there distils over, together with acetic acid, a fruity-smelling oil, which is a mixture of the unaltered alcohol with a ketone, $C^5H^{10}O$, convertible by further oxidation into acetic and carbonic acids. This body is doubtless isopropyl-methyl ketone, or methyl-isobutyryl, $CO\left\{\begin{array}{l}CH^3\\CH(CH^3)^2.\end{array}\right.$

Secondary Amylic Ethers.

These ethers, as well as the corresponding alcohols, are distinguished from the primary amylic compounds by the facility with which they are resolved into amylene (or isoamylene) and the corresponding acids. They may in fact be regarded as amylene compounds intermediate in composition between the primary amyl compounds and the amylene-glycolic compounds. (See ALCOHOLS, p. 65.) The chloride, bromide, and iodide are formed by direct combination of amylene or isoamylene with the haloïd acids.

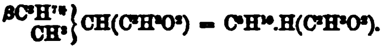
Propyl-methyl-carbinyl Acetate or *Iso-amylene Acetate*,



$$\left.\begin{matrix}C^3H^7\\CH^3\end{matrix}\right\}CH(C^2H^3O^2) = C^5H^{10}.H(C^2H^3O^2),$$

is prepared by adding the corresponding iodide to an equivalent quantity of silver acetate suspended in ether, distilling after 24 hours, agitating the distillate with aqueous sodium carbonate, drying with calcium chloride, and rectifying. It is a colourless liquid, having a pleasant aromatic odour, but not smelling of pears like ordinary amyl acetate. Sp. gr. 0·9222 at 0°. Boils at 133°–135°. Decomposed with some difficulty by caustic potash, yielding propylmethyl-carbinol (Wurtz).

Isopropyl-methyl-carbinyl Acetate or *Amylene Acetate*,



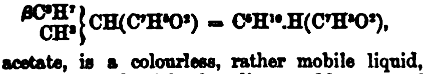
$$\left.\begin{matrix}\beta C^3H^{7}\text{[*]}\\CH^3\end{matrix}\right\}CH(C^2H^3O^2) = C^5H^{10}.H(C^2H^3O^2).$$

Produced by the action of amylene hydriodide on silver acetate. Colourless liquid, lighter than water, boiling at 125°. When kept for some time at 200°, it is resolved into acetic acid and amylene (Wurtz).

Isopropyl-methyl-carbinyl Amylate, $C^{10}H^{22}O = \left.\begin{matrix}\beta C^3H^7\\CH^3\end{matrix}\right\}CH(OC^5H^{11})$, or *Diamylene Hydrate* = $(C^5H^{10})^2.H^2O$, is obtained, as above mentioned, together with the corresponding alcohol, by the action of moist silver oxide on the hydriodide, but in variable quantity. It is an aromatic liquid, differing in odour from its isomeride, primary amylic oxide, and boiling at 160°–165° (the primary ether boils at 176°). Sp. gr. = 0·876 at 0°. Insoluble in water. Resolved by heat into amylene and amylene monohydrate; by gaseous hydriodic acid into water and amylene hydriodide (Wurtz).

Isopropyl-methyl-carbinyl Ethylate, $\left.\begin{matrix}\beta C^3H^7\\CH^3\end{matrix}\right\}CH(OC^2H^5)$; *Ethylene-amylene Hydrate* or *Amylene Ethylate*, $\left.\begin{matrix}C^2H^4\\C^5H^{10}\end{matrix}\right\}H^2O$.—Formed by heating amylene hydrobromide with excess of alcoholic potash (amylene being however the principal product), and separated by washing with water and rectification, finally over sodium. Boils at 102°–103° under a pressure of 742 mm. (the isomeric ethyl-amyl ether, $(C^2H^5)(C^5H^{11})O$, at 112°), and has a sp. gr. of 0·759 at 21°. Heated with hydrobromic acid, it yields primary and secondary amylic bromides (Reboul a. Truchot, *Compt. rend.* lxiv. 1243).

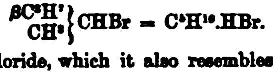
Isopropyl-methyl-carbinyl Benzoate or *Amylene Benzoate*,



$$\left.\begin{matrix}\beta C^3H^7\\CH^3\end{matrix}\right\}CH(C^7H^5O^2) = C^5H^{10}.H(C^7H^5O^2),$$

prepared like the acetate, is a colourless, rather mobile liquid, soluble in water, having a slight benzoic odour, and a faint but disagreeable taste. Sp. gr. 1·007 at 0°. Boils at about 240° (Wurtz).

Isopropyl-methyl-carbinyl Bromide or *Amylene Hydrobromide*:



$$\left.\begin{matrix}\beta C^3H^7\\CH^3\end{matrix}\right\}CHBr = C^5H^{10}.HBr.$$

Prepared like the hydrochloride, which it also resembles in its properties. Sp. gr. 1·227 at 0°. Boils at 113° (corr.). Its vapour-density at different temperatures exhibits variations similar to those of the hydriodide (p. 115) as shown by the following numbers, determined by Wurtz:

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[*] The symbol βC^3H^7 is here used as an abbreviation of $CH(CH^3)^2$.

Temp. (corrected)	V.D.	Temp. (corrected)	V.D.	Temp. (corrected)	V.D.
153°	5·37	193·2°	4·84	262·5°	3·09
158·8	5·18	195·2	4·66	272	3·11
160·5	5·32	205·2	4·39	295	3·19
165	5·14	215	4·12	305·3	3·19
171·2	5·16	225	4·69	314	2·98
173·1	5·18		3·68	319·2	2·88
182·3	5·15	236·5	3·83	360	2·81
185·5	5·12	248	3·30		

Now the calculated vapour-density of the compound, referred to air, is $\frac{60 + 11 + 80}{2} \times 0{\cdot}0693 = 5{\cdot}23$. Hence the compound exhibits a normal vapour-density as high as about 185°, or 72° above its boiling point; but above that temperature the vapour-density diminishes, rapidly between 198° and 250°, and at 360° it is reduced to little more than the half of the calculated density, showing that the compound is resolved at these high temperatures into a mixture of amylene and hydrobromic acid. At the same temperatures hydrobromic acid vapour and amylene may be mixed together without uniting, the mixture not being attended by any perceptible increase of heat. If mixed at 215°–225°, they combine to a small amount, producing a rise of temperature amounting to 0·5°; if mixed between 120° and 130°, they combine in larger proportion, producing a rise of 4° to 5°; and if mixed at 40°, they unite immediately, producing a considerable rise of temperature. All these phenomena show that the anomaly in the vapour-density of this and of similar compounds at high temperatures is due to dissociation (Wurtz, *Compt. rend.* lx. 728; lxv. 1182).

Isopropyl-methyl-carbinyl Chloride, or *Amylene Hydrochloride*, $\left.\begin{matrix}\beta C^3H^7\\ CH^3\end{matrix}\right\}CHCl = C^5H^{10}.HCl$.—Produced by the direct combination of amylene vapour and hydrochloric acid gas, the action being attended with evolution of heat; also by dissolving amylene at ordinary temperatures in 4 vols. absolute alcohol saturated with hydrochloric acid gas, and distilling off the upper layer of liquid after 24 hours (Berthelot, *Compt. rend.* lvi. 700). It is a colourless mobile liquid, having an ethereal odour, boiling at about 90°. Sp. gr. = 0·833 at 0°. Vapour-density at 193° = 3·58 (calc. for a two-volume condensation, 3·688); but at a somewhat higher temperature dissociation occurs, and at 290° the density of the vapour is reduced to that of a mixture of amylene and hydrochloric acid, namely, to 1·808. The amylene and hydrochloric acid recombine in great part on cooling (Wurtz). Amylene hydrochloride treated with aqueous *potash* yields amylene hydrate or isopropyl-methyl carbinol and amylene; with *sodium benzoate* it yields amylene and a large quantity of isopropyl-methyl benzoate; with *sodium acetate*, amylene in rather large quantity, and the corresponding acetate (Berthelot).

Isopropyl-methyl-carbinyl Cyanate, or *Amylene Cyanate*,

$$\left.\begin{matrix}\beta C^3H^7\\ CH^3\end{matrix}\right\}CH(OCN) = C^5H^{10}.HCNO,$$

obtained by treating amylene hydriodide with recently prepared and cooled silver cyanate, is a liquid boiling between 100° and 120°, and having an irritating odour. In contact with *ammonia*, it forms secondary amyl-urea, $C^6H^{14}N^2O = CON^2H^2(CH^3)(C^4H^9)$ [primary amyl-urea being = $CON^2H^3(C^5H^{11})$). This compound crystallises in splendid needles, and when treated with very strong aqueous potash yields carbon dioxide, ammonia, and secondary amylamine or iso-amylamine (p. 116). By *water* or caustic *potash*, amylene cyanate is converted into a mass of crystals, consisting of secondary diamyl-urea, $C^{11}H^{24}N^2O = CON^2H(CH^3)(C^4H^9)(C^5H^{11})$ [primary diamyl-urea being $CON^2H^2(C^5H^{11})^2$] (Wurtz).

Propyl-methyl Carbinyl Iodide, $\left.\begin{matrix}C^3H^7\\ CH^3\end{matrix}\right\}CHI$, or *Iso-amylene Hydriodide*, $C^5H^{10}.HI$, is produced by heating ethyl-allyl (isoamylene) with hydriodic acid, or by the action of iodine and phosphorus on propyl-methyl carbinol (p. 112). It has a sp. gr. of 1·537 at 0° and 1·5219 at 11°. Boils at 129° (Wurtz).

Isopropyl-methyl-carbinyl Iodide, $\left.\begin{matrix}\beta C^3H^7\\ CH^3\end{matrix}\right\}CHI$, or *Amylene Hydriodide*, $C^5H^{10}.HI$, is produced by heating ordinary amylene with concentrated hydriodic acid. It boils at 130° under the ordinary atmospheric pressure (primary amyl iodide at 146°), and at 50°–55° in a vacuum. Sp. gr. = 1·522 at 0°. Its vapour-density, even at temperatures but little above its boiling point, falls below the calculated number, indicating a commencement of decomposition, and at higher temperatures the vapour-density approaches continually to that of a mixture of amylene and hydriodic acid; thus:

Temperature	Vapour-density Air = 1.	Hydrogen = 1.
160°	5·73	82·7
210°	4·06	67·3
262°	4·38	63·2

Half the molecular weight of the compound $C^5H^{11}I$ is $\frac{60 + 11 + 127}{2} = 99$.

With *sodium*, amylene hydriodide yields chiefly amylene and hydrogen. With *silver-acetate* mixed with ether, a brisk reaction takes place, even at 0°, the liquid becoming hot, and yielding secondary amyl acetate, together with amylene and acetic acid:

$$C^5H^{10}\begin{cases}H\\I\end{cases} + AgOC^2H^3O = AgI + C^5H^{10}\begin{cases}H\\OC^2H^3O\end{cases}$$

and

$$C^5H^{10}\begin{cases}H\\OC^2H^3O\end{cases} = C^5H^{10} + HOC^2H^3O.$$

Moist *silver oxide* acts in a similar manner, forming silver iodide, secondary amyl alcohol, amylene, and water. *Aqueous ammonia* heated with the hydriodide to 100° in a closed tube displaces the amylene, and forms only a small quantity of the hydriodide of an organic base, which yields a platinochloride crystallising in golden yellow scales. *Alcoholic potash* liberates amylene (Wurtz).

Tertiary Amyl Alcohol or **Ethyl-dimethyl Carbinol.** $C\begin{cases}(CH^3)^2\\C^2H^5\\OH\end{cases} = (CH^3)^2(C^2H^5).COH$ (Popoff, *Ann. Ch. Pharm.* cxlv. 292).—A mixture of 1 mol. chloropropionyl and 1 mol. zinc-methyl yields needle-shaped crystals of the compound $(CH^3)^2(C^2H^5).CCl$, from which by decomposition with water the tertiary alcohol is obtained, the reaction being precisely analogous to that by which tertiary butyl alcohol is prepared from zinc-methyl and acetyl chloride (p. 66). The alcohol is separated by distillation and addition of a strong solution of potassium carbonate, shaken up with a concentrated solution of acid sodium sulphite, and dried with fused potash and caustic baryta. It boils between 98·5° and 102°, smells very much like trimethyl carbinol, does not solidify at −17°, merely becoming more viscid and syrupy. By oxidation with potassium dichromate and dilute sulphuric acid it yields nothing but acetic acid.

AMYL HYDRIDE or **QUINTANE.** C^5H^{12}.—This saturated hydrocarbon, the fifth of the paraffin or marsh-gas series, C^nH^{2n+2}, is found in American petroleum, of which it constitutes the portion boiling at 30° (Pelouze a. Cahours); it is also found in Boghead naphtha (C. Gr. Williams, *Chem. Soc. J.* xv. 130), and in light coal-tar oil obtained from Wigan cannel-coal (Schorlemmer, *ibid.* 419). It is produced: *α.* By the action of water on zinc-amyl:

$$Zn(C^5H^{11})^2 + 2H^2O = ZnH^2O^2 + 2C^5H^{12}.$$

β. By heating equal volumes of amyl iodide and water to 140° in a sealed tube with excess of zinc (Frankland, *Ann. Ch. Pharm.* lxxiv. 47):

$$2C^5H^{11}I + H^2O + Zn^2 = ZnI^2.ZnO + 2C^5H^{12}.$$

γ. Together with amylene and its polymerides by heating amyl alcohol with zinc chloride.—*δ.* Together with amylene, as a product of the decomposition of diamyl, in the action of zinc on dry amyl iodide:

$$C^{10}H^{22} = C^5H^{12} + C^5H^{10}.$$

The mixture of amyl hydride and amylene formed in these and other reactions may be separated by means of fuming sulphuric acid, which dissolves the amylene, but not the amyl hydride.

Amyl hydride from American petroleum has a sp. gr. 0·628 at 18° and boils at 30° (Pelouze a. Cahours); sp. gr. 0·6263 at 17°, boiling point 34° (Schorlemmer, *Proc. Roy. Soc.* xv. 131). Amyl hydride readily absorbs *chlorine*, forming (together with more highly chlorinated products) amyl chloride, $C^5H^{11}Cl$, boiling at 102°, like that obtained from amyl alcohol (Pelouze a. Cahours). By prolonged action of the chlorine a thickish liquid is obtained, which begins to boil at 180°, and yields between 230° and 240° a liquid having the composition $C^5H^8Cl^4$, and converted by alcoholic potash into trichloramylene, $C^5H^7Cl^3$ (Bauer, *Compt. rend.* li. 572).

AMYL SULPHOXIDE. $C^{10}H^{22}SO = (C^5H^{11})^2SO$.—Produced by carefully dropping amyl sulphide, $(C^5H^{11})^2S$, into fuming nitric acid, and precipitating the solution with water. It then separates as a light yellow oil, solidifying, when washed with sodium carbonate, to a crystalline mass, which may be washed with water and recrystallised from ether. On leaving the still coloured crystals to drain in a funnel, the coloured portion runs away, and the purer compound remains. It forms stellate groups of needles melting at 37°–38°, insoluble in water, easily soluble in strong sulphuric and in fuming nitric acid, from which solutions it is precipitated by water; easily soluble also in alcohol and in ether. It gives off acid vapours at 100°, and is decomposed by distillation, evolving stinking sulphuretted products; is completely oxidised by heating with chromic acid, iodic acid, and other oxidising agents; reduced by zinc and dilute sulphuric acid to amyl monosulphide. Hydriodic acid decomposes it at ordinary temperatures, and more readily when heated, with separation of iodine, and formation of a brown oil insoluble in water. Not altered by ethyl iodide, amyl iodide, or zinc-ethyl (Saytzeff, *Ann. Ch. Pharm.* cxxxix. 354).

AMYLAMINES. Ordinary amylamine, $C^5H^{13}N$, being derived from the amylic alcohol of fermentation, contains the radicle isobutyl $CH^2CH(CH^3)^2$, and is represented by the formula

$$C\left\{\begin{array}{l}CH^2CH(CH^3)^2\\H^2\\NH^2\end{array}\right.\qquad\text{or}\qquad N\left\{\begin{array}{l}CH^2CH^2CH(CH^3)^2\\H\\H.\end{array}\right.$$

It is produced, together with formic acid, by the action of acids—hydrochloric acid for example—on amyl cyanide (Hofmann, *Jahresb.* 1867, p. 364):

$$C^5H^{11}CN + 2H^2O = C^5H^{13}N + CH^2O^2.$$

According to Limpricht (*Bull. Soc. Chim.* [2] viii. 363), a mixture of amyl cyanate and cyanurate, decomposed by potash, forms an oily and a watery layer, the former consisting of amyl alcohol, the latter of a mixture of amylamine, diamylamine, and triamylamine.

Secondary Amylamine or *Isoamylamine.* $C^5H^{13}N = C\left\{\begin{array}{l}CH(CH^3)^2\\CH^3\\H\\NH^2\end{array}\right.$ or $N\left\{\begin{array}{l}CH(CH^3)[CH(CH^3)^2]\\H\\H\end{array}\right.$.—This base, discovered by Wurtz (*Bull. Soc. Chim.* [2] vii. 243), is produced by heating secondary amyl urea (p. 113) in a flask of very hard glass with strong potash mixed with solid potassium hydrate, decanting the liquid which takes the place of the crystals of the urea, and distilling it over caustic baryta. The isoamylamine then distils over at 78·5°. Its density at 0° is 0·755. It has an ammoniacal odour, precipitates cupric salts, but does not redissolve the precipitated cupric hydrate. Its vapour strongly heated in contact with baryta yields combustible gases and a small quantity of barium cyanide. *Bromine* in contact with excess of the concentrated solution of this base forms a hydrobromide of the base and a heavy yellow brominated liquid, $C^{15}H^{12}BrN$, which cannot be distilled. The *hydrochloride*, $C^5H^{13}N.HCl$, crystallises in efflorescent scales, and may be obtained in rather large quadratic octohedrons by pouring ether into the concentrated alcoholic solution. The *platinochloride*, $2C^5H^{14}NCl.PtCl^4$, is very soluble in water and in alcohol, and forms fine crystals, derived from a monoclinic prism. The *aurochloride*, $C^5H^{14}N.AuCl^3$, forms large yellow crystals, also belonging to the monoclinic system.

AMYLENE or **QUINTENE.** C^5H^{10}.—This hydrocarbon, originally obtained by dehydrating amyl alcohol with zinc chloride, is also produced: in the decomposition of amyl chloride by melting potash, or by passing the vapour of that compound over lime heated to dull redness:

$$2C^5H^{11}Cl + CaO = CaCl^2 + H^2O + 2C^5H^{10};$$

in the decomposition of amyl iodide by zinc amalgam in sealed tubes; of amylene hydrate or secondary amyl alcohol by heat; of amylene hydriodide by moist silver oxide, ammonia, silver acetate, &c. (p. 115); of amylene dibromide, by copper and water under certain circumstances; in the dry distillation of amyl sulphates, acetates, and butyrates, also of oleic acid, resin, Boghead coal, and other organic bodies.

To prepare amylene, 1 pt. of fused zinc chloride is drenched with ⅔ pt. amyl alcohol, and the liquid, after several days' contact and frequent agitation, is distilled, the action beginning at 70°–80°, and the distillation being continued till the temperature rises to 130°–140° and the liquid begins to froth. The distillate contains amylene, water, undecomposed amyl alcohol, and polymerides of amylene; it is redistilled in the water-bath, and the distillate is dehydrated, and rectified over sodium. The residue contains di-, tri-, and tetra-amylene (Bauer, *Wien. Akad. Ber.* xliv. [2] 87; *Jahresb.* 1861, p. 659). See also Linnemann (*Ann. Ch. Pharm.* cxliii. 350).

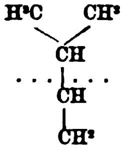
Amylene boils at 33° to 34°. Sp. gr. = 0·66277 at 0°; 0·6549 at 10° (Buff, *Ann. Ch. Pharm. Suppl.* iv. 143).

Iso-amylene or *Ethyl-allyl*, $C^2H^5.C^3H^5$, a hydrocarbon isomeric with the amylene above described, is produced by the action of zinc-ethyl on allyl-iodide:

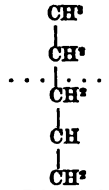
$$Zn(C^2H^5)^2 + 2C^3H^5I = ZnI^2 + 2C^5H^{10}.$$

When a mixture of 1 mol. zinc-ethyl and 2 mol. allyl-iodide is heated to 100° in a sealed tube, a violent action takes place, zinc iodide separates out, and on opening the tube a large quantity of gas escapes, whilst the iodide is saturated with a liquid. On distilling off this liquid, heating it for some days in a sealed tube with potassium, and then subjecting it to fractional distillation, allyl passes over first, forming the principal product, then between 25° and 32° chiefly amyl hydride, and between 32° and 39° ethyl-allyl or iso-amylene mixed with amyl hydride. These two hydrocarbons are separated by treatment with bromine and distillation, the amyl hydride, which does not unite with the bromine, passing off at a comparatively low temperature, the bromisoamylene at about 175° (Wurtz, *Ann. Ch. Pharm.* cxxiii. 202).

The constitution of iso-amylene is shown by its mode of formation; ordinary amylene has not been formed synthetically, but its formation from primary amyl alcohol, and its conversion into secondary amyl alcohol or methyl-isopropyl carbinol (p. 112) show that it has the constitution of vinyl-isopropyl: $C^2H^3.C^3H^7$.



Vinyl-isopropyl or amylene.



Ethyl-allyl or iso-amylene.

Amylene differs by 2 at. hydrogen from the saturated hydrocarbon C^5H^{12}, and is capable of uniting directly with 2 at. bromine, chlorine, and other univalent radicles, also with 1 mol. HCl, HBr, &c., and thereby forming saturated compounds of the type C^5H^{12}. It is therefore a diatomic or bivalent radicle; but, like most other radicles of this class, it possesses considerable stability in the free state, and is capable of giving up a portion of its hydrogen in exchange for other radicles, thereby forming substitution-products of its own type, e.g. C^5H^9Cl, C^5H^9Br, &c.; and these again can take up Cl^2, Br^2, HCl, &c., also forming saturated compounds. On the other hand, amylene bromide, $C^5H^{10}Br^2$, heated with alcoholic potash, gives up 2 mol. hydrobromic acid, and is reduced to quintine or valerylene, C^5H^8, which is a quadrivalent radicle capable of forming saturated compounds, like $C^5H^8Br^4$, and unsaturated (bivalent) compounds, like $C^5H^8Br^2$; moreover, this last-mentioned compound is reduced by treatment with alcoholic potash to quintone or valylene, C^5H^6, which is a sexvalent radicle (v. 982).

The following reactions relate chiefly to ordinary amylene; those of iso-amylene, so far as they have been studied, are analogous:—

1. Amylene is not altered at 360°, but decomposes partially when heated in a glass vessel to the softening point of the glass, yielding traces of acetylene and tar, also hydrocarbons of the series C^nH^{2n}, viz. propylene and butylene, and ethers belonging to the series C^nH^{2n+2} (Berthelot, *Ann. Ch. Phys.* [4] ix. 442). Acetylene is also formed in the imperfect combustion of amylene (Berthelot).

2. Amylene is not decomposed by heating to 300° with aqueous *zinc chloride*, but fused zinc-chloride at 100° converts it partially into diamylene and other polymerides (Bauer, Berthelot).

3. Strong *sulphuric acid* acts in a similar manner, but more quickly (Bauer), the liquid dividing into two portions, the lower of which contains an acid isomeric with amylsulphuric acid, and another corresponding to isethionic acid (Berthelot, *Ann. Ch. Pharm.* cxxviii. 311). At 100° part of the amylene is carbonised (Bauer).

4. Amylene heated with a solution containing 4 to 8 per cent. *potassium dichromate* and a sufficient quantity of *sulphuric acid* is oxidised to acetic and carbonic acids (Chapman a. Thorp). Wurtz obtained from amylene by this mode of oxidation the same products as from amylene hydrate (p. 112). *Potassium permanganate* acts in the same manner as the chromic acid mixture (Chapman a. Thorp). Truchot (*Compt. rend.* lxiii. 274) obtained formic, acetic, and propionic acids; he also observed an odour of butyric acid. According to Berthelot (*Compt. rend.* lxiv. 36), a cold solution of potassium permanganate produces volatile acids, oxalic, malonic, succinic, and perhaps pyrotartaric acid. When amylene is left for a week in contact with a highly concentrated solution of *hydrogen dioxide* in hydrochloric acid, amylene hydrochloride is produced, and may be extracted by ether. The remaining liquid, when freed from hydrochloric acid by silver oxide and concentrated, forms a bitter syrup, which when treated with chlorine bisulphide, yields amylene hydrochloride, and therefore contains hydrated oxide of amylene (Carius, *Ann. Ch. Pharm.* cxxix. 167). Respecting the action of fuming nitric acid and nitrogen tetroxide on amylene, see i. 208, 209.

5. With *bromine*, amylene forms chiefly amylene bromide, $C^5H^{10}Br^2$, likewise bromamylene bromide, $C^5H^9Br.Br^2$ (Reboul, *Compt. rend.* lviii. 105–8).

6. Amylene cooled at first to –15°, and afterwards gently heated, quickly absorbs *chlorine*, with slight evolution of hydrochloric acid, and the product, washed with dilute alkali and dried by calcium chloride, yields on fractional distillation the following compounds: 1. Chloramylene, C^5H^9Cl, of sp. gr. 0·9992 at 0°, and boiling at 90°–95° (in small quantity).—2. Amylene dichloride, $C^5H^{10}Cl^2$, of sp. gr, 1·2219 at 0°, boiling at 145° (in larger quantity).—3. Chloramylene dichloride, $C^5H^9Cl.Cl^2$, by cooling of the portion which goes over between 160° and 190°: white feathery crystals purifiable by sublimation.—4. Dichloramylene chloride, $C^5H^8Cl^2.Cl^2$, a limpid liquid of sp. gr. 2·4292, boiling at 220°–230°; produced in considerable quantity by the action of chlorine on amylene at 100°; not completely dechlorinated even by heating with alcoholic potash to 120°–130° (Bauer, *Zeitschr. f. Chem.* 1866, pp. 380, 667).

7. *Stannic chloride* heated with excess of amylene to 100° in a sealed tube, is reduced to stannous chloride, and converts a portion of the amylene, partly into chloramylene, partly into amylene dichloride. The excess of amylene is at the same time converted into polymeric modifications (Bauer a. Klein, *Zeitschr. f. Chem.* [2] iv. 380).

8. Amylene unites with *hydrochloric* and *hydrobromic acids* less readily than propylene (Berthelot, *Compt. rend.* xliv. 1350); also with hydriodic acid (Wurtz). According to Morkownikoff (*Zeitschr. f. Chem.* [2] ii. 502), it absorbs hydrobromic and hydriodic acids as rapidly as water, hydrochloric acid less quickly; unites also with hydrocyanic acid.

9. It combines readily with *hypochlorous acid*, ClOH, forming amylenic chlorhydrin, $C^5H^{10}.Cl(OH)$ (Carius, p. 121). On agitating it with *iodine*, mercuric oxide, and water, hypoïodous acid is produced, which converts the amylene into amylenic iodhydrin, $C^5H^{10}.I(OH)$ (Lippmann, p. 121).

10. With *carbonyl chloride* (phosgene) amylene becomes hot and forms white fumes, condensing to a pungent liquid, which is not decomposed by contact with water for several days. This liquid yields by distillation amylene and dichloramylene, formed by the free chlorine in the phosgene gas, and between 90° and 100° a very strong-smelling product, consisting of leucic chloride, $C^5H^{10}OCl^2$, formed by direct addition of carbonyl chloride: $C^5H^{10} + COCl^2 = C^5H^{10}OCl^2$ (Lippmann, *Ann. Ch. Pharm.* cxxix. 81).

11. With *phosphorus pentachloride*, amylene becomes heated, and converted, without evolution of hydrochloric acid, into a nearly dry mass containing phosphorous acid, hydrochloric acid, and dichloramylene (Guthrie, *Ann. Ch. Pharm.* cxxi. 108). With *chlorine bisulphide* it unites directly, forming the compound $(C^5H^{10})^2S^2Cl^2$; with brown chloride of sulphur, $(S^2Cl^2 + SCl^4)$, it forms $C^5H^{10}SCl^2$ (Guthrie, i. 209).

12. *Cyanogen iodide* heated with excess of amylene, decomposes it, forming brown products (Erlenmeyer, *Zeitschr. Ch. Pharm.* 1865, p. 545).

COMPOUNDS OF AMYLENE.

The additive compounds of amylene may be divided into two groups, viz.,

a. Those formed by addition of 1 molecule of a haloïd acid, HCl, HBr, &c., and others formed therefrom by substitution of hydroxyl, OH, acetyl, OC^2H^3O, &c., for the haloïd element. These are the secondary amylic compounds, discovered by Wurtz, e.g.,

Amylene Hydrochloride, or Methyl-isopropyl-carbinyl Chloride	$C^5H^{10}.HCl$
Amylene Monohydrate, or Methyl-isopropyl Carbinol	$C^5H^{10}.HOH$
Amylene Mono-acetate or Methyl-isopropyl-carbinyl Acetate	$C^5H^{10}.HOC^2H^3O$

They have already been described, together with the corresponding methyl-propyl compounds derived from iso-amylene or ethyl-allyl, under AMYL ALCOHOLS and ETHERS (pp. 111–115).

β. Compounds formed by addition of 2 at. bromine, chlorine, or other univalent radicles, or 1 at. oxygen, sulphur, or other bivalent radicles, to 1 mol. amylene: these are the amylene-glycolic compounds, e.g.,

Amylene Dichloride	$C^5H^{10}Cl^2$
Amylene Hydrato-chloride or Amylenic Chlorhydrin	$C^5H^{10}\begin{cases}Cl\\OH\end{cases}$
Amylene Dihydrate or Amylenic Glycol	$C^5H^{10}(OH)^2$
Amylene Acetato-chloride or Amylenic Acetochlorhydrin	$C^5H^{10}\begin{cases}Cl\\OC^2H^3O\end{cases}$
Amylene Diacetate	$C^5H^{10}(OC^2H^3O)^2$
Amylene Oxide	$C^5H^{10}O$

Several of these compounds are described in vol. i. pp. 208, 209; the following have been more recently discovered, or further investigated.

Amylene Dibromide. $C^5H^{10}Br^2$.—Produced by the action of bromine on amylene (Cahours, *Compt. rend.* xxxi. 291), or on amylene monohydrate (Wurtz). To prepare it, bromine is added in a fine stream to amylene till the colour remains constant. The product, after washing with dilute potash, then with water, and drying, passes over on distillation, mostly between 170° and 180°, but not without loss of hydrobromic acid, so that it is best to interrupt the distillation at 160°; the residual impure bromide may then be used for the preparation of amylene glycol (Wurtz, *Ann. Ch. Phys.* [3] lv. 458).

Amylene bromide is converted by alcoholic potash, chiefly into monobromamylene (Cahours), but a very small portion is converted by loss of Br^2 into amylene, and another small portion by loss of H^2Br^2 into valerylene, C^5H^8 (Reboul, *Ann. Ch. Pharm.* cxxxiii. 84). With *silver-acetate* it forms amylene diacetate (Wurtz). An alcoholic solution of *potassium acetate* acts upon it at 100° only after addition of glacial acetic acid, and even then but slowly, forming chiefly bromamylene, C^5H^9Br, with a small quantity of amylene diacetate (Bauer, *Bull. Soc. Chim.* 1860, p. 148). With *sodium ethylate* it yields bromamylene and amyl alcohol; with *zinc*, *sodium*, or *potassium*, bromamylene, amylene, and hydrogen (Bauer). Treated with *silver oxalate* under petroleum, it yields amylene, carbon dioxide, and silver bromide:

$$C^5H^{10}Br^2 + C^2Ag^2O^4 = C^5H^{10} + 2CO^2 + 2AgBr$$

(Golowkinsky, *Ann. Ch. Pharm.* cxi. 252).

Derivatives of Amylene Dibromide.

Monobromamylene, C^5H^9Br, formed by heating amylene dibromide with alcoholic potash, is a colourless mobile liquid turning brown on exposure to the air, boiling at 100°–110° (Bauer, *Ann. Ch. Pharm.* cxx. 167; *Zeitschr. Ch. Pharm.* 1861, p. 590); at 117°–118°; sp. gr. 1·22 at 19° (Linnemann, *Ann. Ch. Pharm.* cxliii. 351). It unites with 2 at. bromine, forming $C^5H^9Br.Br^2$, and with chlorine, forming the compound $C^5H^9Br.Cl^2$ in white crystals, but many other products are formed at the same time (Bauer). *Alcoholic potash* at 140° abstracts HBr, and forms valerylene, C^5H^8 (Reboul). Bromamylene distilled with *silver cyanate* yields a compound which forms with ammonia crystals of amyl-urea (Cahours a. Hofmann, *Ann. Ch. Pharm.* civ. 309). *Zinc-ethyl* heated with bromamylene to 130° for 96 hours forms a small quantity of zinc bromide, a gas, and a few drops of a liquid boiling below 40°, probably amylene (Wurtz, *ibid.* cxxiii. 202). Olevinsky (*Zeitschr. Ch. Pharm.* 1861, p. 674) obtained a light liquid having an alliaceous odour and boiling at 70°–80°.

Bromamylene Dibromide. $C^5H^9Br^3 = C^5H^9Br.Br^2$.—On dropping bromine into bromamylene, the liquid soldifies, with hissing and evolution of heat, to a red-brown mass, which may be purified by pressure and recrystallisation from ether (Bauer, *loc. cit.*). This compound is also formed, together with amylene dibromide, on treating amylene with bromine (Reboul, *Compt. rend.* lviii. 1058). It forms white needles having the odour and taste of camphor. When heated it sublimes, with partial decomposition, but without fusion.

Treated with *alcoholic potash*, it yields bromamylene, C^5H^9Br, dibromamylene, $C^5H^8Br^2$, and an ethylate, $\left.\begin{matrix}C^5H^8Br\\C^2H^5\end{matrix}\right\}O$, which boils at 177°–180°, and is capable of taking up 2 at. bromine. The body thus formed, $\left.\begin{matrix}C^5H^8Br^3\\C^2H^5\end{matrix}\right\}O$, is converted by alcoholic potash into another ethylate, $\left.\begin{matrix}C^5H^5\\C^2H^5\end{matrix}\right\}O$, a liquid lighter than water, boiling at 125°–130°, and uniting with bromine, iodine, and concentrated haloïd acids (Reboul).

The alcoholic solution of bromamylene dibromide heated with *silver acetate* yields the diacetate $\left.\begin{matrix}(C^2H^3O)^2\\(C^5H^8Br)''\end{matrix}\right\}O$, which when saponified by fused and pulverised potassium hydrate, yields bromamylene dihydrate, or bromamylene glycol, $\left.\begin{matrix}C^5H^8Br\\H^2\end{matrix}\right\}O^2$; and this last body heated to 100° in a sealed tube with potash yields amylic glycerin, $\left.\begin{matrix}(C^5H^9)'''\\H^3\end{matrix}\right\}O^3$ (Bauer, *Zeitschr. Ch. Pharm.* 1861, p. 673).

Amylene Dibenzoate, $C^5H^{10}.(C^7H^5O^2)^2$, produced by the action of silver benzoate on amylene dibromide, forms large colourless shining laminæ, soluble in alcohol and ether, melting at 123° (Meyer, *Compt. rend.* lix. 444).

Amylene Dichloride. $C^5H^{10}Cl^2$ (Guthrie, *Chem. Soc. Qu. J.* xiv. 128; Bauer, *Zeitschr. f. Chem.* [2] iv. 380, 667).—1. A mixture of phosphorus pentachloride and amylene forms a nearly dry mass, from which water, after twelve hours' standing, separates amylene dichloride as an oily layer, while hydrochloric and phosphorous acids remain in solution. The amylene dichloride is purified by washing, drying, and rectification (Guthrie).—2. The dichloride may also be prepared by passing chlorine through amylene, cooled at first to −15°, and then gradually heated to the boiling point of the resulting liquid. The product, washed with alkaline water, dried, and subjected to fractional distillation, gives off between 90° and 95°, monochloramylene, and at about 145° amylene dichloride, which at higher temperatures becomes mixed with more highly chlorinated products (Bauer, p. 118).—3. It is formed, together with polymerides of amylene, by the action of stannic chloride on amylene and on amyl alcohol (Bauer a. Klein, p. 118).

Amylene dichloride is a liquid of sp. gr. 1·058 at 9° (Guthrie); 1·2219 at 0° (Bauer). Boils at 141°–147° (Guthrie); at 145° (Bauer).

When valeraldehyde is heated with rather more than an equivalent quantity of phosphorus pentachloride, and the product is mixed with water, washed, dried, and distilled, there passes over a light mobile oil consisting of an isomeride of amylene dichloride. This compound has a sp. gr. of 1·05 at 24°, and boils at 130°. It is insoluble in water, soluble in alcohol and ether, and is decomposed by alcoholic potash (Ebersbach, *Ann. Ch. Pharm.* cvi. 265).

Chloramylene, C^5H^9Cl, is formed, together with other chlorine-compounds (p. 118), by the action of chlorine on amylene. It boils at 90°–95°, has a sp. gr. of 0·9992 at 0°; vapour-density = 3·82 (calc. 3·62) (Bauer).

Chloramylene Dichloride, $C^5H^9Cl.Cl^2$, is produced, together with chloramylene and amylene dichloride, by the action of chlorine upon amylene, and constitutes the portion of the product which boils between 160° and 190°. This distillate yields on cooling white feathery crystals, which may be purified by pressure and sublimation. The mother-liquor exhibits the same proportion of chlorine as the crystals, and therefore perhaps contains an isomeric compound (Bauer, *J. pr. Chem.* c. 42).

Dichloramylene Dichloride. $C^5H^8Cl^4 = C^5H^8Cl^2.Cl^2$.—Produced by prolonged treatment of amyl hydride with chlorine, and separated from the very viscid product by fractional distillation, passing over between 230° and 250°, but is decomposed by repeated distillation. It is a thick, heavy, colourless liquid decomposed by alcoholic potash, with formation of trichloramylene. Soluble in alcohol and ether, insoluble in water (Bauer, *Jahresb.* 1860, p. 405).

A compound isomeric or identical with this is formed, together with amylene dichloride and other products, by the action of chlorine on amylene, and passes over on fractional distillation between 220° and 230°. It is a transparent colourless liquid, of sp. gr. 1·4292 at 0°; decomposes partially on distillation. Alcoholic potash separates from it a large quantity of potassium chloride, but does not form a non-chlorinated and distillable product even at 130° (Bauer, *J. pr. Chem.* c. 43).

Trichloramylene, $C^5H^7Cl^3$, is produced by treating dichloramylene dichloride with alcoholic potash, and boils at about 200° (Bauer).

Amylenic Chlorhydrin, $C^5H^{10}\left\{\begin{matrix}Cl\\OH\end{matrix}\right.$, described at p. 208, vol. i., as produced by the action of hydrochloric acid on amylene glycol, is also readily formed by direct addition of hypochlorous acid, ClOH, to amylene. A solution of hypochlorous acid of 1 or 2 p. c. ClHO (containing also mercuric oxychloride and excess of mercuric oxide) is gradually mixed in a glass vessel having a ground stopper, with amylene in the proportion of rather more than 1 molecule of the latter to 2 at. chlorine. As soon as the odour of the acid ceases to be perceptible, the aqueous solution of the amylenic chlorhydrin is filtered, freed from dissolved mercury by hydrogen sulphide, then neutralised with sodium carbonate, and shaken up with ether. The ethereal solution dehydrated with potassium carbonate, and freed from ether by evaporation over the water-bath, leaves the amylenic chlorhydrin as a colourless liquid, which may be further purified by standing over oil of vitriol, and one subsequent distillation. It has a powerful odour, like that of valeric acid, is heavier than water, and soluble therein, and is precipitated from the aqueous solution by salts. It distils easily with aqueous vapour, boils, when quite pure at 155°, and has a vapour density of 4·218 (calc. 4·245). It dissolves mercuric chloride in considerable quantity, and cannot be separated by distillation from this solution without decomposition, inasmuch as mercurous chloride is produced on heating the liquid (also from the aqueous solution). By potash it is resolved into potassium chloride and amylene oxide (Carius, *Ann. Ch. Pharm.* cxxvi. 195).

Amylenic Iodhydrins.—When amylene is shaken up with iodine and mercuric oxide, mercuric iodide and hypoïodous acid, HIO, are formed, which latter combines directly with the amylene, forming an iodhydrin, which is heavier than water, is decomposed by distillation, and when treated with silver acetate yields acetic acid, silver iodide, and amylene oxide. When iodine, mercuric oxide, and amylene are introduced into absolute alcohol, the iodine disappears, forming mercuric iodide and several iodhydrins which cannot be distilled except in a vacuum. An iodhydrin thus prepared was found to contain $\left.\begin{matrix}(C^5H^{10})^2\\C^2H^5\end{matrix}\right\}\begin{matrix}O\\I\end{matrix}$; another, which could not be distilled, gave, with silver acetate, a mixture of amylenic acetates, from which, by fractional distillation, the following compounds were separated:

A: boiling at 150°.	B: boiling at 165°.
$\left.\begin{matrix}C^5H^{10}\\C^5H^{10}\\C^2H^5\end{matrix}\right\}\begin{matrix}O^2\\C^2H^3O\end{matrix}$	$\left.\begin{matrix}C^5H^{10}\\C^2H^5\end{matrix}\right\}\begin{matrix}O\\C^2H^3O\end{matrix}$

The body B, which was formed in the largest quantity, yielded, by heating with hydriodic acid to 150°, the iodides of ethyl and amyl (Lippmann, *Zeitschr. Ch. Pharm.* 1867, p. 17).

Amylene Iodocyanide, $C^5H^{10}.ICy$, is obtained in an impure state, by adding amylene drop by drop to cyanogen iodide. It is a brown liquid, which distils over with water, and may be decolorised by acid sodium sulphite. With alcoholic potash at the boiling heat it yields ammonia and leucic acid, or an isomer thereof:

$$\underset{\substack{\text{Amylene}\\\text{iodocyanide.}}}{C^5H^{10}.ICN} + 2KOH + H^2O = KI + NH^3 + \underset{\substack{\text{Potassium}\\\text{leucate.}}}{C^6H^{11}KO^3}$$

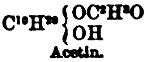
(Erlenmeyer, *Zeitschr. Ch. Pharm.* vi. 545).

Amylene Bisulphide, $C^5H^{10}S^2$, is produced by boiling diamylene sulphochloride for some hours with zinc-granules in a flask provided with a reflex condenser. On distilling off the greater part of the alcohol, and washing the residue with water, the bisulphide rises to the surface as an oil, which may be dried and rectified. The pure compound is a colourless oil, having a sp. gr. of 0·907 at 13°, and boiling at about 200° (Guthrie, *Chem. Soc. Qu. J.* xiv. 128).

Amylene Sulphocarbonate, $C^5H^{10}CS^3$, obtained by the action of an alcoholic solution of amylene bromide on sodium sulphocarbonate, is a somewhat viscid liquid of more or less yellow-brown colour, and sp. gr. = 1·073 (Hüsemann, *Jahresb.* 1862, p. 434).

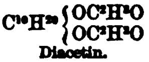
AMYLENES, POLYMERIC. *Diamylene.* $C^{10}H^{20}$ (Balard, *Ann. Chim. Phys.* [3] xii. 320; Bauer, *Rép. Chim. pure*, 1862, p. 3; *Bull. Soc. Chim.* 1863, p. 332; 1867, viii. 341; Berthelot, *Chimie organique fondée sur la Synthèse*, ii. 700; and *Compt. rend.* lvi. 1242).—This body, representing a double molecule of amylene, was discovered by Balard, who named it paramylene. It is produced, together with other hydrocarbons, by the action of strong sulphuric acid or zinc chloride on amyl alcohol, or on amylene. It also occurs amongst the products of the action of zinc-ethyl on allyl iodide. It is a liquid having a sp. gr. of 0·7777 at 0°, and boiling at 165°.

When *bromine* is added to a cooled ethereal solution of diamylene, a bromide, $C^{10}H^{20}Br^2$, is obtained, very easily decomposed by heat. On adding the ethereal solution of this bromide by small portions to dry silver acetate mixed with acetic acid, and heating the mixture in the water-bath, a mixture of the *acetin* and *diacetin* of diamylenic glycol is obtained, viz.,



$$C^{10}H^{20}\begin{cases}OC^2H^3O\\OH\end{cases}$$

Acetin.



$$C^{10}H^{20}\begin{cases}OC^2H^3O\\OC^2H^3O\end{cases}$$

Diacetin.

When the acetate thus obtained by distillation is heated with pulverised potassium hydrate, it yields diamylene oxide, $C^{10}H^{20}O$ (isomeric with capric aldehyde), in the form of a light liquid boiling at 170°–180°, and having a vapour-density of 5·361 (calc. 5·401). This oxide is insoluble in water, soluble in alcohol and ether, reduces ammoniacal silver nitrate, and has an odour of rue (Bauer). When diamylene cooled to −17° is treated with a current of *chlorine*, the temperature being gradually raised to 11° and ultimately to 140°, the liquid, which had at first turned brown, becomes colourless, and when washed with alkaline water and distilled, yields at 240°–250° chlorinated diamylene chloride, $C^{10}H^{19}Cl.Cl^2$, soluble in alcohol and ether, and having a density of 1·1638 at 0°. This chloride heated in closed vessels with alcoholic potash yields chlororutylene, $C^{10}H^{17}Cl$, and if the action of the potash be repeated on this body, potassium chloride is again separated, indicating the formation of the compound $C^{10}H^{16}$ (Bauer).

Diamylene directly treated with *bromine* forms an unstable oil, $C^{10}H^{19}Br.Br^2$. By oxidation with *potassium dichromate* and *sulphuric acid*, it yields a green oxygenated non-acid oil, boiling between 130° and 200°, an acid product containing acetic acid and an oily acid, and a tarry residue, which appears to contain an acid boiling between 215° and 225° (Walz, *Zeitschr. f. Chem.* [2] iv. 315).

Diamylene disulpho-dichloride, $C^{10}H^{20}S^2Cl^2$.—This compound, obtained by treating chlorine disulphide with excess of amylene, was discovered by Guthrie, and is described in vol. i. p. 209 as *disulphochloride of amylene*. The formula there given contains an uneven number of univalent atoms, and should therefore be doubled.

The compound chars when heated, giving off hydrochloric acid, sulphydric acid, and other sulphuretted products. The alcoholic solution heated with *zinc* forms amylene bisulphide, $C^5H^{10}S^2$; if an acid is present, sulphur is likewise removed. Fuming *nitric acid* attacks it violently, forming sulphuric, hydrochloric, oxalic, and a sulpho-acid; and by incomplete action, a heavy green oil agreeing approximately with the formula $C^{10}H^{18}S(NO^2)^4$.

With *potassium acetate*, diamylene sulphochloride appears to form the compound $C^{10}H^{20}.(C^2H^3O)^2.S^2$. With *zinc-ethyl* it forms a compound whose composition is approximately represented by the formula $(C^7H^{15})^2S^2$ (? heptyl bisulphide).

With alcoholic *potassium cyanide* it forms diamylene dithiodicyanide, $C^{10}H^{20}Cy^2S^2$, a liquid having a sp. gr. of 1·07 at 13°. With alcoholic *potassium sulphocyanate* it yields diamylene tetrathiodicyanide, $C^{10}H^{20}Cy^2S^4$, a liquid of sp. gr. 1·16 at 13° (Guthrie, *Chem. Soc. J.* xiii. 35; xiv. 128).

Triamylene, $(C^{15}H^{30})''$, is produced, together with several other products, by heating amyl alcohol or amylene with zinc chloride (p. 117). On removing the products which distil below 160°, and dissolving the residue in water, an oil rises to the surface which when distilled yields triamylene between 240° and 250°, and tetramylene between 390° and 400°. Both these products must be rectified over sodium.

Triamylene is a colourless oil having an odour of turpentine, a sp. gr. of 0·8139, and boiling at 248°. Vapour-density = 7·6 (calc. 7·4). It is insoluble in water, soluble in alcohol, but not in all proportions, insoluble in ether. Burns with a white sooty flame. Reacts with bromine like diamylene. The bromide, $C^{15}H^{30}Br^2$, acts violently on silver acetate even at −15°, producing triamylene acetate, $C^{15}H^{30}.(C^2H^3O^2)^2$, which is decomposed by potash, yielding potassium acetate, water, and benylene, $C^{15}H^{28}$ (Bauer, *Wien. Akad. Ber.* xliv. [2] 87; *Jahresb.* 1861, p. 659; *Ann. Ch. Pharm.* cxxxvii. 249). Triamylene bromide is also converted into benylene by heating to 100° with alcoholic potash: $C^{15}H^{30}Br^2 + 2KOH = 2KBr + 2H^2O + C^{15}H^{28}$. The formation of benylene from triamylene is similar to that of rutylene from diamylene (Bauer a. Verson, *Zeitschr. f. Chem.* [2] iv. 501).

Tetramylene. $(C^{20}H^{40})''$.—Discovered by Balard (*Ann. Ch. Phys.* [3] xii. 320), who named it *metamylene*. It is formed simultaneously with triamylene in the reactions above mentioned, and purified by rectification in a vacuum. It is a thick brownish oil, having a sp. gr. of 0·871 at 0°, and boiling between 390° and 400°. Dissolves with difficulty in alcohol, more easily in ether (Bauer).

AMYL-ETHYL SULPHIDE. $\left.\begin{matrix}C^5H^{11}\\C^2H^5\end{matrix}\right\}S$. *Amyl sulphethylate* or *Ethyl sulphamylate.*—This compound, prepared by the action of amyl alcohol on ethyl disulphophosphate (ii. 548), was found by Carius to boil at 132°–132·5°. Linnemann prepared it by the action of amyl iodide on potassium sulphide in alcoholic solution, and found it to boil between 130° and 140°. According to Saytzeff (*Zeitschr. f. Chem.* [2] vi. 105), it boils at 158°–159°, whether prepared by the heating amyl chloride with sodium sulphethylate (mercaptide) or ethyl iodide with sodium sulphamylate. It is oxidised by nitric acid to amyl-ethyl sulphoxide, $(C^5H^{11})(C^2H^5)SO$, a thick, yellowish, oily liquid, which is not distillable without decomposition, and solidifies in a freezing mixture to a crystalline mass, melting even below 0°. By zinc and dilute sulphuric acid the sulphoxide is reduced to amyl-ethyl sulphide (Saytzeff, *Ann. Ch. Pharm.* xxxix. 354).

AMYLULMIC ACID. See Methulmic Acid, iii. 984.

AMYRIN. A constituent of arbol-a-brea resin (i. 354), and probably also of elemi resin (ii. 483).

ANACAHUITTA. A wood of unknown botanical origin, lately imported into Europe from Mexico, and said to yield preparations useful in pulmonary disorders. The bark and wood yield to alcohol and cold water only a small quantity of extractive matter, together with iron-greening tannin. The aqueous decoction yields on standing a large quantity of calcium oxalate, which is deposited in the parenchyma cells, and may likewise be isolated by agitating the bast with ether. The wood leaves 2·9 p. c., the bast about 20 p. c. ash, consisting almost wholly of calcium carbonate (A. Buchner, *Chem. Centr.* 1861, p. 447). The wood is said also to contain a volatile oil which unites with acid sodium sulphite, a tannic acid resembling catechutannic acid, gallic acid, a yellowish resin, arabin, uncrystallisable sugar, grape-sugar, a tasteless volatile body which crystallises in warty masses, and a bitter substance crystallising in white needles which does not precipitate platinic chloride or phosphomolybdic acid (*Jahresb.* 1861, p. 771).

ANAËROBIES. Pasteur's name for those infusoria which live, or at least act as ferments, only when excluded from the air: they are also called zymic ferments (from ζύμη, yeast); on the other hand, those which, like *Monas* and *Bacterium*, require the presence of oxygen, are called Aërobies or Azymic ferments.

ANALYSIS, INORGANIC. *Disintegration of Insoluble Substances.*—The ordinary method of treating substances insoluble in water and acids, by fusion with an alkaline carbonate in a platinum or porcelain crucible, involves the risk either of destroying the platinum vessel by the action of reducible metals which may possibly be present, or of contaminating the fused mass with silica and alumina derived from the porcelain crucible; moreover, with an ordinary gas-burner or blowpipe it is not easy to raise a porcelain crucible to the high temperature required for the fusion. These inconveniences may be avoided by a method introduced by Bloxam (*Chem. Soc. J.* [2] iii. 226), which consists in causing the heat to be applied *inside* the mass to be fused. For this purpose the substance under examination is intimately mixed with 2 pts. sodium carbonate and 14 pts. of a mixture composed of 1 pt. finely pulverised charcoal and 6 pts. saltpetre; the mixture is placed in a thin porcelain dish or clean iron tray, and set on fire with a glowing slip of wood. The deflagration is completed in two or three seconds, and a well-fused mass remains, which is easily detached from the cooled dish, and may then be boiled, first with water, and then with acids for the extraction of the soluble constituents. This method is effectual for the disintegration of quartz-sand, pipe-clay, fluor-spar, and indeed of all insoluble substances, except chrome-iron ore. Barium sulphate (heavy spar) is so completely decomposed by it that the process may be advantageously applied to the preparation of soluble barium salts. Tin-stone, flint-glass, crown-glass, silver chloride, lead sulphate, and cryolite are also perfectly decomposed, felspar only partially. In cases when it is not desired to search for sulphates, the disintegration may also be advantageously effected by deflagrating a mixture of 1 pt. of the insoluble substance with 4 pts. sodium carbonate, 4 pts. saltpetre, and 10 pts. of finely pulverised gunpowder.

To search for alkalis, the insoluble substance is deflagrated with seven times its weight of a mixture of 1 pt. sulphur and 6 pts. barium nitrate in a porcelain crucible; the cooled mass is well boiled with water; and the filtrate, after being freed from the dissolved baryta, is examined for alkalis in the usual way. Flint-glass, felspar and cryolite thus treated give up the whole of their alkali.

W. Clarke (*Sill. Am. J.* [2] xlv. 173) disintegrates refractory minerals, such as chrome-iron ore, rutile, &c., by mixing them, finely pulverised, with 3 pts. sodium fluoride in a platinum crucible, covering the mixture with a layer of acid potassium sulphate (12 pts.) and heating the crucible over a Bunsen's lamp till the mixture attains a state of tranquil fusion. The fused product is almost always perfectly soluble in water, especially if it be moistened after cooling with sulphuric acid, and heated again. When the presence of alumina does not interfere with the analysis, cryolite may be used instead of sodium fluoride. The author prepares sodium fluoride by boiling cryolite with caustic soda in an iron vessel, washes the gelatinous sodium fluoride thereby separated with cold water, and purifies it by crystallisation.

Schönn (*Zeitschr. f. Chem.* [2] v. 664; vi. 279) decomposes insoluble substances by fusing them in a steel crucible with potassium or sodium. For the detection of iron, however, a separate portion must be fused in a glass tube.

Qualitative Analysis of Metallic Solutions containing only the more ordinary metals without the use of Hydrogen Sulphide or Ammonium Sulphide (Zottnow, *Pogg. Ann.* cxxx. 324).—1. Lead, silver, and mercurosum are precipitated by *hydrochloric acid*, and the chlorides are separated in the usual way.

2. The filtrate is treated with *sulphuric acid*, which throws down lead, calcium (in part), strontium, and barium. Calcium sulphate is extracted from the precipitate by water; the small quantity of lead sulphate may be dissolved out by ammonium tartrate; and the strontium and barium sulphates may be separated by known methods.

3. One-fourth of the liquid filtered from the precipitated sulphates is treated with *barium hydrate*, the liquid boiled, and the vapour tested for ammonia; on precipitating the excess of barium by ammonium carbonate, then evaporating the filtered solution, and calcining, a residue is obtained containing the fixed alkalis.

4. The remaining portion of the liquid filtered from the sulphates is treated with *zinc* in a flask fitted with a gas-delivery-tube, drawn out at the end, and the evolved hydrogen is tested for arsenic and antimony. The zinc at the same time precipitates tin, antimony, mercury, copper, cadmium, and bismuth [also gold, platinum, and the allied metals], in the metallic state; this precipitation is much facilitated by placing a piece of platinum foil in contact with the zinc. The precipitated metals, after being washed, are treated with nitric acid, which dissolves them all, except tin and antimony, which are converted into stannic and antimonic acids [and gold, platinum, &c., which remain in the metallic state]. One portion of the resulting solution is tested for mercury with stannous chloride; the rest is boiled with soda; and the resulting precipitate is treated, after washing, with ammonia and sal-ammoniac, which dissolves copper and cadmium, and leaves bismuth in the state of hydrate. The ammoniacal filtrate contains copper and cadmium, which are easily recognised, the former by potassium ferrocyanide, the latter by caustic soda.

5. The solution containing the metals not precipitated by zinc is oxidised with *nitric acid*. Iron may then be recognised by treating one portion of the liquid with *potassium sulphocyanate*. Another portion is neutralised by ammonia, and shaken up with *barium carbonate*, which precipitates chromium and aluminium as hydrates: the precipitate is boiled with soda, a small quantity of potassium permanganate being added to oxidise the chromic hydrate; and the filtered solution is examined for chromic acid and alumina in the usual way. (If the liquid contains phosphoric or boric acid, ferric chloride is added before precipitating with barium carbonate.)

6. The solution filtered from the barium carbonate is treated with sulphuric acid to remove dissolved barium, then treated with *ammonium carbonate*, which precipitates manganese, together with any remaining portion of lime; the filtrate still retains magnesium, nickel, and cobalt. The magnesium is precipitated by sodium phosphate; the filtrate is evaporated to dryness; the residue dissolved in hydrochloric acid; the cobalt precipitated by potassium nitrite and acetic acid; and the nickel from the filtrate by soda.

7. To search for zinc, the solution separated from the chlorides and sulphates (1, 2) is boiled with caustic soda; the filtrate is treated with ammonium chloride and carbonate as long as ammonia continues to escape; and the liquid again filtered is examined for zinc with potassium ferrocyanide.

J. Thomson (*Zeitschr. anal. Chem.* vi. 183) recommends the following method for the qualitative separation of the metals which are not precipitated by hydrogen sulphide from solution in hydrochloric acid (iron, aluminium, chromium, zinc, nickel, cobalt, manganese, barium, strontium, calcium, and magnesium). The solution, containing excess of hydrochloric acid, and heated with nitric acid or potassium chlorate, is first mixed with dilute sulphuric acid, which separates barium and strontium as sulphates. The filtrate, mixed with a large quantity of sodium acetate, yields, on addition of sodium phosphate (containing free acetic acid) in the cold, a precipitate containing nothing but ferric and aluminic phosphates. From the filtrate, hydrogen sulphide throws down the zinc, and after approximate saturation with sodium carbonate, also the cobalt and nickel. The solution, again filtered, is boiled with sodium hypochlorite, whereby manganese dioxide is precipitated (together with lime and magnesia), while chromic acid remains dissolved. The precipitated manganese dioxide is freed from lime and magnesia by dilute acetic acid.

Influence of Fixed Organic Substances on the Precipitation of Metallic Oxides from Saline Solutions by Alkalis.—The following results have been obtained by H. Grothe (*J. pr. Chem.* xcii. 175):—1. The alterations produced in the reactions of different metallic solutions with alkalis by the presence of fixed organic bodies exhibit great diversities, scarcely any two metallic bodies being similarly affected, so that these alterations do not afford properties characteristic of groups of metallic oxides, but rather of individual oxides.—2. Of non-volatile organic substances, citric acid acts most strongly in modifying these reactions; then follows tartaric acid; then sugar, starch, and gum, which, however, act but feebly, and require to be added in large excess.—3. The precipitating action of ammonia is diminished by these bodies much more than that of sodium carbonate.—4. Solutions which are not precipitated in presence of fixed organic bodies by alkaline hydrates or carbonates are for the most part precipitated by alkaline orthophosphates, pyrophosphates, arsenates, and borates. —5. Sodium orthophosphate may be used as a reagent in nearly all cases in which the precipitation of a metallic oxide is hindered by the presence of non-volatile organic substances.

The table on the following page exhibits the reactions of the more important metallic salts with ammonia, and with carbonate, borate, phosphate, pyrophosphate, arsenate, and borate of sodium, in presence of tartaric acid, citric acid, and sugar: 'p.' denotes perfect precipitation; 'i.' imperfect precipitation; a dash, no precipitation.

ANALYSIS, INORGANIC, BY FLAME REACTIONS. (Bunsen, *Ann. Ch. Pharm.* cxxxviii. 257; *Phil. Mag.* [4] xxxii. 81.)—Almost all the reactions which can be performed by means of the blowpipe may be accomplished with far greater ease and precision in the flame of the non-luminous gas-lamp. This flame, moreover, possesses several peculiarities which render it available for reactions by which the smallest traces of many substances occurring mixed together can be detected with certainty when the blowpipe and even still more delicate methods fail.

I. THE STRUCTURE OF THE NON-LUMINOUS GAS-FLAME.

The gas-lamp with non-luminous flame used for these reactions is represented in fig. 1, and must be made, exactly to scale, 3½ times as large as the drawing. It must be furnished with a cap at *a* for closing and opening the draught-holes, so as to regulate the supply of air for every dimension of the flame. The conical chimney *d d d d* (fig. 2) must also be made of such a size that the flame burns perfectly steady. Fig. 2 represents this flame of half its natural size. It is composed of the following three chief divisions:—A. *The dark cone, a a a,* containing the cold unburnt gas mixed with about 62 per cent. of atmospheric air. B. *The flame-mantle, a c a b,* formed of the burning coal-gas mixed with air. C. *The luminous point, a b a,* not seen when the lamp is burning with the draught-holes open, but obtained of the size required for the reactions by closing these holes up to a certain point.

The following six points in the flame are used in the reactions:—

1. *The base of the flame* lies at *a*; its temperature is comparatively very low, as here the burning gas is cooled by the upward current of cold air, and much heat is absorbed by the cold end of the metal tube. If mixtures of flame-colouring substances are held in this part of the flame, it is often possible to vaporise the most volatile constituent, and thus in the first few moments to obtain tints which cannot be observed at higher temperatures, because they then become masked by colours produced by the volatilisation of the remaining substances.

Table of Precipitation referred to on p. 125.

		Ammonia.	Sodium Carbonate	Sodium Ortho-phosphate.	Sodium Pyro-phosphate.	Sodium Arsenate.	Sodium Borate.
Aluminium salts	Tartaric acid . .	—	—	p.	p.	p.	p.
	Citric acid . . .	—	—	—	—	—	—
	Sugar	i.	i.	p.	p.	p.	p.
Manganous salts	Tartaric acid . .	—	p.	i.	i.	p.	p.
	Citric acid . . .	p.	i.	p.	p.	p.	p.
	Sugar	p.	p.	p.	p.	p.	p.
Manganic salts	Tartaric acid . .	—	p.	p.	i.	p.	p.
	Citric acid . . .	—	p.	i.	p.	p.	i.
	Sugar	p.	i.	p.	p.	p.	p.
Zinc salts	Tartaric acid . .	i.	i.	p.	p.	p.	p.
	Citric acid . . .	—	i.	p.	p.	p.	p.
	Sugar	p.	p.	p.	p.	p.	p.
Nickel salts	Tartaric acid . .	—	—	i.	i.	i.	i.
	Citric acid . . .	—	i.	i.	i.	i.	i.
	Sugar	i.	i.	i.	i.	i.	i.
Cobaltous salts	Tartaric acid . .	—	i.	i.	i.	i.	i.
	Citric acid . . .	i.	i.	i.	i.	i.	i.
	Sugar	—	p.	p.	p.	i.	p.
Uranic salts	Tartaric acid . .	—	—	—	—	—	—
	Citric acid . . .	—	—	—	—	—	—
	Sugar	i.	—	—	—	—	—
Ferrous salts	Tartaric acid . .	—	i.	p.	p.	p.	p.
	Citric acid . . .	—	—	—	—	—	—
	Sugar	—	p.	p.	p.	p.	p.
Ferric salts	Tartaric acid . .	—	—	p.	p.	p.	p.
	Citric acid . . .	—	—	—	—	—	—
	Sugar	—	p.	p.	p.	p.	p.
Cupric salts	Tartaric acid . .	—	—	p.	i.	p.	p.
	Citric acid . . .	—	—	—	—	—	—
	Sugar	i.	p.	p.	p.	p.	p.
Cadmium salts	Tartaric acid . .	—	i.	p.	p.	p.	p.
	Citric acid . . .	i.	p.	p.	p.	p.	p.
	Sugar	—	p.	p.	p.	p.	p.
Lead salts	Tartaric acid . .	i.	p.	p.	p.	p.	p.
	Citric acid . . .	i.	p.	p.	p.	p.	p.
	Sugar	—	i.	p.	p.	p.	p.
Bismuth salts	Tartaric acid . .	—	p.	p.	p.	p.	p.
	Citric acid . . .	—	p.	p.	p.	p.	p.
	Sugar	—	p.	p.	p.	p.	p.
Chromic salts (green solution)	Tartaric acid . .	i.	—	—	—	i.	—
	Citric acid . . .	p.	—	—	—	—	—
	Sugar	i.	—	—	—	p.	—
Chromic salts (violet solution)	Tartaric acid . .	p.	p.	p.	p.	p.	p.
	Citric acid . . .	p.	p.	p.	p.	p.	p.
	Sugar	p.	p.	p.	p.	p.	p.

2. *The zone of fusion* lies at β, somewhat above the first third of the flame in height, and midway between the inner and outer limits of the mantle at the point where the flame is thickest. This is the point in the flame which possesses the highest temperature, and it is therefore used in testing substances as regards their melting-point, their volatility, their emissive power, as well as for all processes of fusion at high temperatures.

3. *The lower oxidising flame* lies at γ, in the outer margin of the zone of fusion, and is especially suitable for the oxidation of substances dissolved in beads of fused salts.

4. *The upper oxidising flame* at ε is formed by the highest point of the non-luminous flame, and acts most powerfully when the draught-holes of the lamp are wide open.

FIG. 1.

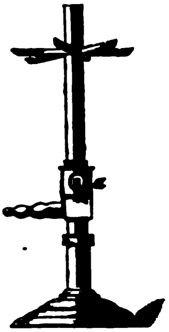
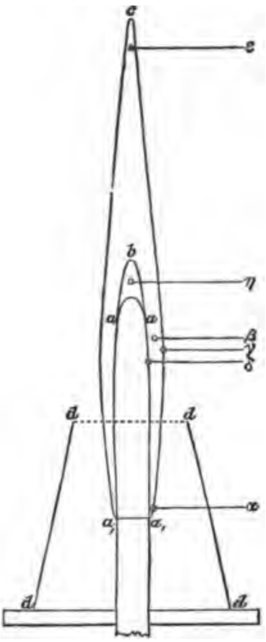


FIG. 2.



This flame is suited for the oxidation of larger portions of substance, for roasting off volatile oxidation-products, and generally for all those cases of oxidation in which an excessively high temperature is not needed.

5. *The lower reducing flame* lies at δ, on the interior edge of the mantle next to the dark central zone. As the reducing gases at this point are mixed with unburnt atmospheric oxygen, many substances remain here unaltered which become deoxidised on exposure to the upper reducing flame. This point of the flame gives, therefore, very valuable reactions which cannot be obtained with the blowpipe. It is especially available for reductions on charcoal, and in beads of fused salts.

6. *The upper reducing flame* is formed by the luminous point η, produced over the dark zone when the admission of air is lessened by the gradual closing of the draught-holes (fig. 1, *a*). If this luminous point is made too large, it will be found that a test-tube filled with cold water and held there becomes covered with a film of lampblack: this ought never to occur. This flame contains no free oxygen, is rich in finely divided incandescent carbon, and hence it possesses far greater reducing powers than the lower reducing flame. It is especially available for reducing metals when it is desired to collect them in the form of films.

II. Method of Examination in the various parts of the Flame.

A. *Behaviour of the Elements at High Temperatures.*—This is one of the most important reactions which can be employed for the detection and separation of substances. The possibility of producing, with the flame of the lamp alone, a temperature as high as or higher than that of the blowpipe, depends upon the condition that the radiating surface of the heated body be made as small as possible. The arrangement for bringing the substances into the flame must therefore be on a very small scale. The platinum wire upon which the substance is heated must scarcely exceed the thickness of a horsehair, and one decimetre in length of the wire must not weigh more than 0·034 grm. It is impossible to obtain the results hereafter detailed if a thicker wire than this is employed. Substances which act upon platinum, or which will not adhere to the moistened surface of the metal, are held in the flame upon a thin thread of asbestos, of which a hundred may be obtained from one splinter of the mineral. These threads must not exceed in thickness one-fourth of that of an ordinary lucifer-match. Decrepitating substances are ground to the finest powder on a porcelain plate with an elastic knife-blade, and drawn up on to a moistened strip of one square centimetre of filter-paper. If the paper is then burnt, being held with the platinum forceps, or, better, between two rings of fine platinum wire, the sample remains as a coherent crust, which now may without difficulty be heated in the flame.

If the substance requires to be heated in the flame for a long time, the holder (fig. 3) is used. The arm *a* is fastened to the carrier A, so fixed on the stand by a spring (as seen at B) that it can be moved both horizontally and vertically. The glass tube (fig. 4) is held on this arm *a*, and the fine platinum wire fused on to the tube thus held in the flame. The splinters of asbestos are stuck into the glass tube *b*, which slips into the holder, and may then be moved with the carrier A. The carrier B carries a spring-clamp for holding test-tubes which have to be heated for a considerable time in a particular part of the flame. The little turntable C contains nine upright supports to hold the wire tubes (fig. 4) employed in the experiments. By means of these arrangements a particle of the substance under examination is brought into the flame, and its behaviour in the coldest and hottest parts of the flame is ascertained, the substance being examined with a lens after each change of temperature.

The following six different temperatures can be obtained in the flame, and these points may be judged of by observing the tints attained by the thin platinum wire :—

1. Below a red heat. 2. Commencing red heat. 3. Red heat. 4. Commencing white heat. 5. White heat. 6. Strong white heat.

It is scarcely necessary to remark that these different temperatures must not be ascertained by the glow of the substances themselves, as the luminosity of different bodies depends not only upon the temperature, but also mainly upon their specific power of emission.

The following phenomena are observed when a sample of a substance is heated :—

1. *Emission of Light.*—The emissive power of substances is ascertained by placing them on the platinum wire in the hottest part of the flame. The sample is of weak emissive power when it is less luminous than the platinum wire, of a mean emissive power when both appear about equally luminous, and of strong emissive power when the intensity of the light which it emits is greater than that from the platinum. Most solid bodies emit a white light, others (as, for instance, erbia) coloured light.

Some bodies, such as many osmium, carbon, and molybdenum compounds, volatilise and separate out finely divided solid matter, which renders the flame luminous. Gases and vapours always exhibit a smaller power of emission than fused substances, and these generally less than solid bodies. The form of the substance under examination must always be noted, as the emissive power depends upon the nature of the surface; thus compact alumina, obtained by slowly heating the hydrate, possesses only a moderate emissive power, whereas the porous oxide prepared by quick ignition of the sulphate possesses a high power of emission.

2. *The melting point* is determined by using the six different temperatures already mentioned. At every increase of temperature the bead is examined with the lens to see whether the volume is decreased or increased, whether bubbles are given off on melting, whether, on cooling, the bead is transparent, and what changes of colour it undergoes during the action of the heat or on afterwards cooling.

3. *The volatility* is ascertained by allowing equally heavy beads of the substance, placed on a platinum wire, to evaporate in the zone of fusion, and observing the time,

by means of a metronome, which the bead takes to volatilise. The point at which the whole of the substance is converted into vapour can be ascertained with great accuracy, often to a fraction of a second, by the sudden disappearance of the coloration of the flame. The platinum wire upon which the substance is weighed is protected from the moisture of the air by insertion in a tube. If we know the weight of the tube and wire, the right weight of substance can easily be attached, either by volatilising a portion or by fusing some more substance on to the bead, and thus making it lighter or heavier. The experiments are best made with one centigramme of substance. The position in the flame where the highest constant temperature exists can be found by moving a fine platinum wire, fixed on a stand and bent at its point at a right angle, slowly about the zone of fusion, and noting the point where it glows most intensely. The beads to be volatilised are then most carefully brought into the flame at the same distance from the point of this wire. Care must also be taken that the dimensions of the flame do not undergo change from alterations in the pressure of the gas whilst the experiments are going on. As a measure of volatility, it is convenient to take the time needed to evaporate one centigramme of sodium-chloride. If we call this time t^0, and the time of volatilisation of the same weight of another substance t^1, the volatility of this substance, compared with that of common salt, is

FIG. 3.

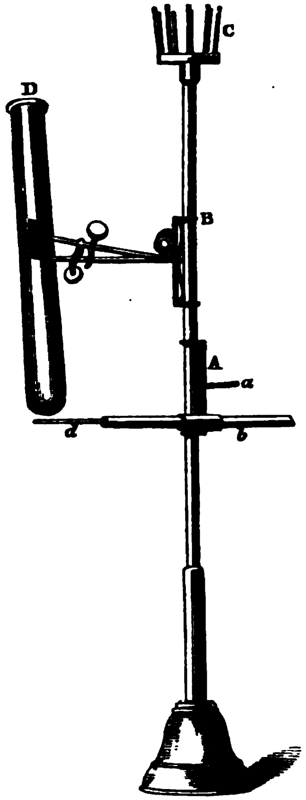
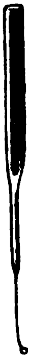


FIG. 4.



$$v = \frac{t^0}{t^1}.$$

The following examples are taken from experiments of Dr. Hurtzig, to which are added the chlorides of cæsium and rubidium :—

	Time of evaporation	Volatility
Sodium chloride.	84·25	1·000
Sodium sulphate	1267·0	0·066
Lithium carbonate	736·5	0·124
Potassium sulphate	665·2	0·127
Sodium carbonate	632·0	0·133
Potassium carbonate	272·0	0·310
Lithium chloride	114·0	0·739
Potassium chloride	65·4	1·288
Sodium chloride.	48·8	1·727
Potassium bromide	41·0	2·055
Rubidium chloride	38·6	2·183
Sodium iodide	35·7	2·360
Cæsium chloride	31·3	2·717
Potassium iodide	29·8	2·828

It must not be forgotten that the relations of these numbers are altered if the temperature of evaporation and the weight of the substance are changed.

4. *Flame Coloration.*—Many substances which volatilise in the flame may be detected by the peculiar kinds of light which their glowing gases emit. These colorations appear in the upper oxidising flame when the substance causing them is placed in the upper reducing flame. Mixtures of various flame-colouring substances are tested in the lowest and coldest part of the flame; and here it is often possible to obtain for a few moments the peculiar luminosity of the most volatile of the substances unaccompanied by that of the less volatile constituents.

B. *Oxidation and Reduction of Substances.*—In order to recognise substances by the phenomena exhibited in their oxidation and reduction, and to obtain them in a fit state for further examination, the following methods are employed:—

1. *Reduction in glass tubes* is especially employed for the detection of mercury, and for the separation of sulphur, selenium, phosphorus, &c., when in combination with sodium or magnesium. A stock of very thin glass tubes is prepared, each 2 to 4 millims. in width and 3 centims. in length: forty of these are easily made out of one ordinary-sized test-tube, by softening the glass before the blowpipe, and then drawing it out until the requisite size of tube is obtained. This long tube is then cut up with a diamond into pieces 6 to 8 centims. long, each of which is again divided into two over the lamp, and the closed ends are neatly rounded. The sample having been finely powdered with a knife-blade on a porcelain plate, is treated in a tube either by itself, or with a mixture of carbon and soda, or with sodium or magnesium. A piece of magnesium wire a few millims. in length is for this purpose pushed down into the powdered sample contained in the glass tube; and the sodium is carefully freed from rock-oil and rolled out between the fingers to a small cylinder, which is then surrounded by the powdered substance. The best form of carbon is the soot from turpentine, which has been deposited upon the outside of a basin filled with cold water. As soon as the small tube containing the perfectly dry sample has been heated to the point of fusion of the glass, when generally an ignition inside the tube is noticed, it is allowed to cool and then placed upon the porcelain plate, covered with a piece of paper, and crushed to powder with the knife, for the purpose of further examining the products of reduction.

2. *Reduction on Splinters of Charcoal.*—In this way the metal can be obtained in small globules, or as a porous mass, from quantities often less than a milligramme of the sample.

A transparent crystal of sodium carbonate is brought near to the outside of the flame, and a common wooden lucifer-match is rubbed over two-thirds of its length with the drops of fused salt. If the match is then turned upon its axis through the flame, the carbonised wood becomes surrounded with a crust of solid sodium carbonate, which, on heating in the zone of fusion, melts and is absorbed by the carbon. A splinter of charcoal is thus obtained, which is prevented from burning by its glaze of soda. A mixture of the substance is then made with the knife upon the hand with one drop of the melted soda-crystal, and a portion of this, of the size of a mustard-seed, is placed upon the point of the splinter. As soon as this has been melted in the lower oxidising flame, it is passed through a part of the dark interior zone to the hotter portion of the lower reducing flame. The point at which the reduction occurs is easily seen by the violent effervescence of the soda; and this is after a time stopped by bringing the splinter into the dark zone. In order to isolate the reduced metal, the end of the splinter is broken off and rubbed up with a few drops of water in a small agate mortar, when the metallic particles are generally visible without removal of the carbon. For further examination, the carbon and soda can be easily removed by several careful washings, and the particles transferred to a small piece of curved glass cut out from an old flask,* in which they are again washed by decantation, the last drops of water removed by suction with a piece of filter-paper, and the metallic particles dried at a moderate heat. A few tenths of a milligramme of the metal is generally sufficient to yield a solution with which all the characteristic precipitations can be accomplished, the reagents being contained in capillary glass threads, dropped into the solution by the milligramme, and the effect thus produced ascertained by examination with a lens. Iron, cobalt, and nickel, which do not fuse to globules on the splinter, are withdrawn from the agate mortar by means of the point of a magnetised blade, washed with water, and dried high above the flame on the point of the knife. If the blade be then tightly drawn between the upper part of the thumb and the lower part of the first finger, and if the point of the blade be then approached to the metallic particles on the finger, they jump from the hand to the blade, forming a brush-like bundle which can be conveniently examined by the lens, and by touching with a melted borax-bead can be transferred in suitable quantities. The portion of metal remaining on the knife is rubbed on to a small piece of filter-paper, a drop of acid added, and the paper warmed over the flame so as to allow the metal to dissolve; this solution can then be further examined with various reagents.

3. *Films upon Porcelain.*—Those volatile elements which are reduced by carbon and hydrogen can be deposited from their compounds as films on porcelain either in the elementary state or as oxides. Such films can be very easily converted into iodides, sulphides, and other compounds, and thus may be made to serve as most valuable and characteristic tests. The films are composed in the centre of a thicker layer, which gradually becomes thinner on all sides until the merest tinge is reached; it is therefore necessary to distinguish between 'thick' and 'thin' parts of the films. Both exhibit in their variation of thickness all the tints of colour characteristic of the substance under different circumstances of division. One-tenth up to one milligramme is in many cases sufficient for these reactions. Many surpass Marsh's arsenic test in delicacy and certainty, and approach in this respect the spectrum-analytical methods.

The following films can be obtained:—

a. Metallic films are prepared by holding in one hand a particle of the substance on an asbestos-thread in the upper reducing flame, which must not be too large, whilst with the other hand a glazed porcelain basin, 1 to 2 decimetres in diameter, filled with cold water, is held close above the asbestos-thread in the upper reducing flame. The metals separate out as dead black or brilliantly black films of varying thickness. Even lead, tin, cadmium, and zinc yield in this way films of reduced metal which by mere inspection cannot be distinguished from the soot separated out on the porcelain by a smoky flame. By means of a glass rod, these films can be touched with a drop of dilute nitric acid containing about 20 per cent. of real acid; and the various degrees of solubility of the films serves as a distinguishing characteristic.

b. Oxide films are obtained by holding the porcelain basin filled with water in the *upper oxidising flame*, the rest of the operation being the same as in the production of the metallic films. If only a very small quantity of the sample can be employed, care must be taken to lessen the size of the flame, in order that the volatile products may not be spread over too large a surface of porcelain.

The film of oxide is examined as follows: α. The colour of the thick and thin film is carefully observed.—β. The reducing action or otherwise of a drop of stannous chloride is noted.—γ. If no reduction occurs, caustic soda is added to the stannous chloride until the precipitated hydrate redissolves, and then it is to be observed whether a reduction occurs.—δ. A drop of perfectly neutral silver nitrate is rubbed over the film with a glass rod, and a current of ammoniacal air is blown over the surface from a small wash-bottle containing ammonia solution, and having the mouth-tube dipping under the liquid and the exit-tube cut off close below the cork. If a precipitate is formed, the colour is observed, and the solubility or alteration, if any, noticed which occurs when the current of alkaline air is continued, or when a drop of ammonia liquor is added.

c. Iodide films are obtained from the oxide films by breathing on the latter upon the cold basin, which is then placed upon a wide-mouthed well-stoppered glass containing fuming hydriodic acid and phosphorous acid derived from the gradual deliquescence of phosphorous iodide. When the mixture no longer fumes, owing to absorption of moisture, it is easy to render it again fuming by adding a little anhydrous phosphoric acid. Other films, often containing both iodides of a metal, and therefore frequently less regular in colour and appearance, may be easily obtained by smoking the oxide film with a flame of alcohol containing iodide in solution, placed upon a bundle of asbestos-threads and held under the basin. If any iodine be condensed on the basin with the hydriodic acid, it can easily be removed by gentle warming and blowing.

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* Watch-glasses crack much too readily to be used for such experiments.

The examination of the film is conducted as follows: α. The solubility of the film is examined simply by breathing upon it when the basin is cooled; the colour then either changes or entirely disappears, the film being dissolved in the moisture of the breath. If the basin be gently warmed, or if it be blown upon for some distance, the film again becomes visible by the evaporation of the moisture in the current of air.—β. The ammonia compound of the iodide is formed by blowing ammoniacal air upon it and noticing whether the colour of the thick and thin films alters quickly, slowly, or not at all. The different colours reappear at once if the basin be held for a few moments over an open bottle containing fuming hydrochloric acid.—γ. The iodide films generally give the same reactions as the oxide films with silver nitrate and ammonia, with stannous chloride, and with caustic soda.

d. The *sulphide film* is most easily obtained from the iodide film by blowing upon it a current of air saturated with ammonium sulphide, and removing the excess of sulphide by gently warming the porcelain. It is advisable to breathe on the film from time to time whilst the current of sulphuretted air is being blown on the basin. The experiments to be made with this film are: α. The solubility or insolubility in water is ascertained by breathing on it, or by adding a drop of water. The sulphides often possess the same colour as the iodide films; they may, however, generally be distinguished by their insolubility on breathing.—β. The solubility of the sulphide in ammonium sulphide is ascertained by blowing or dropping.

4. *Films on Test-tubes.*—Under certain circumstances it is advisable not to collect the film on porcelain, but upon tho outside of a large test-tube; this method is especially used when it is needed to collect larger quantities of the reduction film for the purposes of further examination. The fine asbestos-thread with the sample of substance is held on the glass tube before the lamp so that it is placed at the height of the middle of the upper reducing flame, and the test-tube fixed so that the lowest point is just above the end of the asbestos-thread. If the lamp be now pushed under the test-tube, the substance and the asbestos-thread are in the reducing flame. By repeating this operation the film can be obtained of any wished-for thickness; some pieces of marble are in this case placed in the test-tube, to prevent the water from being thrown out of the tube by percussive boiling.

III. The Reactions of the Elements.

The elements, which can easily be recognised by their flame reactions, are arranged in the following groups and subgroups according to their behaviour in the reducing and oxidising flames:—

A. Elements reducible to metal and deposited in films:
  1. Films scarcely soluble in cold dilute nitric acid—tellurium, selenium, antimony, arsenic.
  2. Films slowly and difficultly soluble in cold dilute nitric acid—bismuth, mercury, thallium.
  3. Films instantly soluble in cold dilute nitric acid—cadmium, zinc, indium.

B. Elements reducible to the metallic state, giving no film:
  1. Not fusible to a metallic bead.
    a. Magnetic—iron, nickel, cobalt.
    b. Non-magnetic—palladium, platinum, rhodium, iridium.
  2. Fusible to metallic beads—copper, tin, silver, gold.

C. Elements most easily separated and recognised as compounds — tungsten, titanium, tantalum and niobium, silicon, chromium, vanadium, manganese, uranium, sulphur, phosphorus.

In the special descriptions of the flame-reactions, the following abbreviations will be used: Fl. c., flame-coloration; Vl., volatilisation; R. f., reduction-film; M. f., metallic-film; O. f., oxide-film; I. f., iodide-film; S. f., sulphur film; Ch. sp., charcoal splinter with soda.

1. *Tellurium compounds.*—Fl. c.: In the upper reducing flame pale blue, whilst the upper oxidising flame appears green. Vl. unaccompanied by any smell. R. f. black, thinnest part blackish brown, dead or bright; heated with concentrated sulphuric acid gives splendid carmine-red colour. O. f. white, invisible or nearly so; stannous chloride colours it black from reduced tellurium; silver nitrate, after blowing with ammoniacal air, yellowish-white. I. f. blackish-brown, thinnest part

brown; disappears momentarily on breathing on it, but not when slightly warmed; reappears on exposure to hydrochloric acid; blackened by stannous chloride. S. f. blackish-brown to black; does not disappear by breathing; soluble in sulphuretted air; reappears on warming or by dry blowing. Ch. sp. yields a sodium-telluride, which, when moistened, leaves a black mark on a silver coin; and if the sample contains much tellurium, gives off a smell of telluretted hydrogen when moistened with hydrochloric acid.

2. *Selenium compounds.*—Fl. c. the bright blue of the corn-flower. Vl. burns, giving off the peculiar putrid smell of selenium. R. f. brick-red to cherry-red, sometimes dead, sometimes bright; heated with strong sulphuric acid, gives an olive-green solution. O. f. white; on addition of stannous chloride, brick-red from liberated selenium; the red colour becomes darker on addition of caustic soda; silver-nitrate gives a white not easily visible coloration, which disappears in a current of ammoniacal air. I. f. brown, contains some reduced selenium, and hence cannot be completely removed either by blowing with ammoniacal air or by breathing. S. f. yellow to orange-red, insoluble in water, soluble in ammonium-sulphide. As the sulphide is prepared from the iodide, it also contains free selenium, and does not give very clear reactions. Ch. sp. gives sodium-selenide, producing a black mark on a silver coin when moistened, and giving rise, if the quantity be not too small, when touched with hydrochloric acid, to red selenium and a smell of seleniuretted hydrogen.

3. *Antimony compounds.*—Fl. c. by treatment in the upper reducing flame, pale green, unaccompanied by smell. Vl. black, sometimes dead, sometimes bright. O. f. white; moistened with perfectly neutral silver-nitrate solution and then blown on by ammoniacal air, it gives a black spot which does not disappear in ammonia. It is unaltered by stannous chloride, either with or without caustic soda. I. f. orange-red, disappearing by breathing, and reappearing by blowing or warming; blown on with ammoniacal air it disappears, but does not return; generally it gives the same reactions as the oxide. S. f. orange-red; the film is difficult to blow away with sulphide of ammonium; returns on blowing with air; insoluble in water. Ch. sp. gives no black stain on silver, but yields a white brittle metallic bead.

4. *Arsenic compounds.*—Fl. c. in upper reducing flame pale blue, giving the well-known arsenical smell. Vl. black, dead or brilliant, thin film brown. O. f. white; touched with perfectly neutral silver-nitrate and then blown with ammoniacal air, it gives a canary-yellow precipitate, soluble in ammonia. Together with the lemon-yellow precipitate, a brick-red one of silver-arsenate occurs when the film has previously been treated with bromine vapour. Stannous chloride with or without soda produces no change. I. f. deep yellow; disappears transiently on breathing, permanently in ammoniacal air; reappears unaltered after the action of hydrochloric acid. S. f. lemon-yellow, disappears easily on blowing with ammonium-sulphide, and reappears on warming or blowing; insoluble in water, and does not disappear on breathing. Ch. sp. yields no metallic bead.

5. *Bismuth compounds.*—Fl. c. bluish, not characteristic. R. f. black, dead or brilliant; thin portion of film brownish black. O. f. light yellow; unaltered by silver-nitrate with or without ammonia; gives no reaction with stannous chloride, but yields black precipitate of bismuth suboxide on addition of caustic soda. I. f. very characteristic, and remarkable for the number of tints which it assumes; the thick part is of a brown or blackish-brown colour, with a shade of lavender-blue; the thin film varies from flesh-coloured to light pink; it easily disappears on breathing, and appears again on blowing; in a stream of ammoniacal air it passes from pink to orange, and on blowing or warming it again attains a chestnut-brown colour; it resembles the oxide-film in its behaviour to stannous chloride and caustic soda. S. f. of a burnt-umber colour, the thin parts of a lighter coffee-brown colour; does not disappear on blowing, and is not soluble in ammonium-sulphide. Ch. sp. metallic bead, yielding, when rubbed in the mortar, bright shining yellowish splinters of metal soluble in nitric acid. The solution gives, with stannous chloride and caustic soda, black bismuth suboxide.

6. *Mercury compounds.*—M. f. mouse-grey, non-coherent, and spreads over the whole basin. To obtain small traces of mercury in the reduced state, the sample is mixed with soda and saltpetre and filled into a thin test-tube 5 to 6 millims. wide and 10 to 20 millims. long. This is held by a platinum wire in the flame, whilst the bottom of the basin filled with cold water is placed close above the open end of the tube. If the quantity of mercury is considerable, the metal collects in the form of small globules which can be seen with a lens, and collected into larger drops by wiping the basin with a piece of moistened filter-paper. O. f. not obtainable. I. f. obtained by breathing on the metallic film and then placing it over a vessel containing moist bromine. It first becomes black and then disappears, but not until

after some time, as mercuric bromide is formed. If the basin be now placed above a vessel of fuming hydriodic acid, a very characteristic carmine-coloured film of mercuric iodide is produced: this is often accompanied by mercurous iodide; but neither of these disappears on breathing, or when blown with ammoniacal air. S. f. black, not altered by breathing or by blowing with ammonium-sulphide. Ch. sp. no reaction.

7. *Thallium compounds.* — F. c. bright grass-green. M. f. black; thin parts coffee-coloured. O. f. colourless; with stannous chloride and soda, as well as with silver-nitrate with or without ammonia, no alteration. I. f. lemon-yellow, does not disappear on breathing, or on blowing with ammoniacal air, or on addition of liquid ammonia. S. f. formed from the oxide, black, and the thin parts bluish-grey; insoluble in liquid ammonium-sulphide. Ch. sp. reduced to a white ductile bead, which quickly oxidises in the air, and is acted upon by hydrochloric acid with difficulty. In addition to the foregoing, there are two metals, viz. tin and molybdenum, which may be classed under the group A 2. These two metals, however, cannot be reduced from all their compounds, and the reduction never takes place easily, owing to their slight volatility; so that it will be better to class them under the groups B 2, B 1, *b*, as they can be best distinguished by the reactions which are characteristic of these groups.

8. *Lead compounds.*—Fl. c. pale blue. R. f. black, dead or brilliant. O. f. bright yellow-ochre coloured; no coloration with stannous chloride and caustic soda, or with silver-nitrate or ammonia. I. f. orange- to lemon-yellow, insoluble on breathing or on moistening; disappears on blowing with ammoniacal air, and appears again on warming. S. f. brownish-red to black; not altered by blowing or moistening with ammonium-sulphide. Ch. sp. grey, very soft ductile metallic bead, soon tarnishing, and slowly but completely soluble in nitric acid.

9. *Cadmium compounds.*—M. f. black; the thin parts brown. O. f. brownish-black, shading off through brown to a white invisible film of suboxide, which is not altered by stannous chloride either alone or with soda, but gives with silver-nitrate a characteristic blackish-blue coloration of reduced metal; does not alter by ammonia. I. f. white, not changed by ammonia. S. f. lemon-yellow, insoluble in sulphide ammonium. Ch. sp., imperfect reduction to a silver-white ductile bead.

10. *Zinc compounds.*—R. f. black, in the thin parts brown. O. f. white, and therefore invisible. To test it, a square centimetre of filter-paper moistened with nitric acid is rubbed over the surface and then rolled up on two rings of fine platinum wire, 3 millims. in diameter, and burnt. If the paper is burnt in the upper oxidising flame at as low a temperature as possible, the ash forms a small solid mass about a square millimetre in area, which can be ignited without fusion, and becomes yellow on gently heating, appearing, however, white on cooling. If this be moistened with a few milligrammes of a very dilute cobalt solution and ignited, it appears of a beautiful green colour on cooling. I. f. white, not easily recognisable either by itself or after blowing with ammoniacal air. S. f. also white, not easily recognised either with or without blowing with ammonium-sulphide. *The reduction of the metal* cannot be accomplished, owing to the volatility of zinc.

11. *Indium compounds.*—Fl. c. intense, and pure indigo-colour. M. f. black, the thin parts brown, either dead or brilliant; instantly disappears in presence of nitric acid. O. f. yellowish-white, scarcely visible; gives no reaction with stannous chloride and silver solution. I. f. also yellowish-white, not visible either with or without ammonia, if present in small quantities only. S. f. also yellowish-white, difficult to see; unaltered by ammonium-sulphide. Ch. sp.; reduction difficult; gives silver-white ductile globules slowly soluble in hydrochloric acid.

12. *Iron compounds.*—Ch. sp., no metallic bead or ductile lustrous particles; the finely divided metal forms a black brush on the end of the magnetised knife-blade; this, when rubbed off on paper and dissolved in a drop of aqua regia, yields a yellow spot when warmed over the flame, which, when moistened with potassium-ferrocyanide, gives a deep coloration of prussian-blue. The yellow spot moistened with caustic soda and then held for a few moments in a vessel with bromine-vapour gives, on a second addition of soda, no coloration of a higher oxide. *Borax bead.*—In the oxidising flame, when hot, yellow to brownish-red; when cold, yellow to brownish-yellow; reducing flame bottle-green.

13. *Nickel compounds.*—Ch. sp.: On pulverising the charcoal the metal is obtained in white, lustrous, ductile particles, forming a brush on the magnetised blade. The metal dissolved in nitric acid on paper gives a green solution, which on moistening with soda, exposure to bromine-vapour, and subsequent addition of soda, gives a blackish-brown spot of nickel-sesquioxide. The ash of the paper, from which the excess of soda has been washed out, can be used for the borax-bead test.

Borax bead.—Oxidising flame greyish-brown or dirty-violet. Upper reducing flame grey from reduced nickel, which often collects to a spongy mass of metal, rendering the bead colourless.

14. *Cobalt compounds.*—By pulverising the charcoal, as with nickel, white ductile lustrous metallic particles are obtained, which form a brush on the magnetic blade. The metal, rubbed off on paper, gives a red solution when moistened with nitric acid; this yields a green colour on addition of hydrochloric acid and drying, which disappears again on moistening. The paper moistened with soda, brought into bromine-vapour and again moistened with soda, yields a blackish-brown spot of cobalt-sesquioxide. This reaction is plainly seen with a few tenths of a milligramme of metal. The paper can also be used, after washing out the soda and burning, for the coloration of the borax bead.

Borax bead.—In the oxidising flame a bright-blue bead, unaltered in the lower reducing flame. The bead when held for some time in the most powerful upper reducing flame, becomes colourless, owing to the separation of metallic cobalt: this separation takes place more rapidly in presence of platinum-ammonium-chloride, when an alloy of nickel and platinum is formed.

15. *Palladium compounds.*—*In the upper oxidising flame* these compounds, heated on a fine platinum wire with soda, yield a grey mass resembling spongy platinum; this yields on trituration silver-white lustrous particles, the red solution of which in nitric acid forms, with a drop of mercuric cyanide, when blown upon by ammoniacal air, a white precipitate soluble in excess of ammonia. The solution is coloured blue, green, and brown by stannous chloride, according to the quantity of the reagent added.

16. *Platinum compounds* yield in *the oxidising flame* with soda a grey spongy mass, giving on trituration white, ductile, lustrous particles. These are insoluble in either nitric or hydrochloric acid alone, but dissolve in a mixture of these acids, forming, if the platinum is pure, a light-yellow solution, which is of a darker colour if rhodium, iridium, or palladium is present. The solution in nitro-muriatic acid gives with mercuric cyanide and ammonia, not a white precipitate, but a light-yellow crystalline precipitate of platinum-ammonium-chloride. Stannous chloride colours platinum compounds yellowish-brown.

17. *Iridium compounds* are likewise reduced to metal when heated with soda in the upper reducing flame, yielding a grey non-lustrous powder, which is not the least ductile, and is insoluble even in aqua regia.

18. *Rhodium compounds* can be distinguished from those of iridium only by the fact that the metallic powder, insoluble in aqua regia, when fused with hydropotassic sulphate, is partially oxidised, giving a rose-coloured solution.

19. *Osmium compounds* give, in the oxidising flame, fumes of volatile osmic acid, possessing an acrid chlorine-like smell and attacking the eyes powerfully.

20. *Gold compounds.*—Traces of gold mixed with large quantities of matrix, can be concentrated and detected only by the old gold-test.[*] In other cases, however, a few tenths of a milligramme can be detected by reduction with soda on a charcoal splinter. The yellow lustrous ductile globules thus obtained can be flattened out to larger golden particles; these do not dissolve in nitric or hydrochloric acid, but are pretty easily dissolved in aqua regia, yielding a light-yellow solution, which, if it is absorbed by a small piece of filter-paper, yields the purple of Cassius when moistened with stannous chloride.

21. *Silver compounds.*—If silver occurs only in traces in slags or complex ores, it can only be detected by the well-known method of cupellation.[†] If, however, the silver compound is not mixed with a very large amount of foreign matter, it can be detected in very minute quantities by reduction with soda on the charcoal splinter. The white ductile beads dissolve easily on warming in dilute nitric acid, and yield silver-chloride with hydrochloric acid, which can then readily be recognised by its behaviour with nitric acid and ammonia. Less than one-tenth of a milligramme of silver can thus be easily detected with certainty.

22. *Copper compounds* yield *on the charcoal splinter with soda* a ductile lustrous metallic bead, easily recognisable by its red copper colour, and by the reaction of its nitric acid solution with potassium ferrocyanide. *With Borax on Platinum Wire.*—Blue bead, not altered to cuprous oxide when heated in the lower reducing flame alone, but on addition of very little tin-salt, forms a reddish-brown bead. If this bead be frequently oxidised and reduced in the flame, a ruby-red transparent bead is obtained; this occurs most readily when the bead is allowed to oxidise very slowly.

23. *Tin compounds.*—*On the charcoal splinter* the tin compounds are easily reduced to white lustrous ductile metallic beads. The flattened particles transferred to the

[*] C. F. Plattner's *Probierkunst*, bearbeitet v. Th. Richter, 1865, p. 541.

[†] *Ibid.* p. 512.

curved glass dissolve slowly in hydrochloric acid; and the solution, when absorbed by paper, gives a red precipitate with selenious, and a black precipitate with tellurous acid dissolved in hydrochloric acid. If to the solution a trace of bismuth-nitrate be added, an excess of soda gives a black precipitate of bismuthous oxide. The metal acted on by nitric acid yields a white powder of insoluble stannic acid. *A borax bead*, containing enough copper-oxide to render it faintly blue, serves as a delicate test to ascertain with certainty the presence of a trace of a tin compound, as the bead placed in the lower reducing flame, as explained above, turns reddish-brown, or forms a clear ruby-red glass.

24. *Molybdenum compounds.—On a charcoal splinter with soda* molybdenum is reduced, though with great difficulty, to a grey powder. In the same way some molybdenum compounds give in the upper reducing flame a film on porcelain which it is very difficult to obtain. Molybdenum is best detected as follows. The sample, finely pulverised with the knife on the porcelain plate, is mixed on the hand with soda, obtained in a pasty state by melting a crystal. The mixture is then transferred to a spiral of fine platinum wire and fused in the flame; the liquid fused mass is then knocked off the wire and allowed to fall upon the plate, when it is digested with two or three drops of water, and the clear supernatant liquid absorbed by three or four strips of filter-paper a few millimetres in breadth. α. One of these strips, on moistening with hydrochloric acid, does not change colour, but on addition of a drop of potassium-ferrocyanide it is coloured reddish-brown. β. If one of the strips be gradually moistened with a few milligrammes of stannous chloride, it is coloured blue either at once or on gently heating; if the tint be yellow or light brown, a few drops of soda solution must be added by a capillary tube until the blue colour appears. γ. A drop of ammonium-sulphide added to the third strip produces a brown coloration; and on addition of hydrochloric acid a brown precipitate is formed, the paper, at the circumference of the drop, often being coloured blue. δ. The yellow phosphate precipitate produced by the nitric acid solution of ammonium-molybdate can also be readily obtained. The borax bead is not very characteristic; in the oxidising flame it is colourless, and in presence of much molybdenum it becomes opaque; in the reducing flame it is dark from reduced molybdenum.

25. *Tungsten compounds.*—The reduction of tungsten can likewise be made on the charcoal splinter with soda, but this method is not available for the detection of the metal. The tungsten compounds are therefore best examined in the mode described under molybdenum, by absorbing the liquid obtained by fusion with soda on some strips of filter-paper. α. One strip is moistened with hydrochloric acid; it remains white, but on heating turns yellow; moistened with ferrocyanide it is unaltered. β. A second strip, touched with stannous chloride, is coloured blue in the cold or on heating. γ. A drop of ammonium-sulphide causes no precipitate either by itself or after addition of hydrochloric acid; the paper becomes, however, blue- or greenish-coloured, especially on warming.

26. *Titanium compounds* give with microcosmic salt in the oxidising flame a colourless bead which turns of a pale amethystine colour in the reducing flame. On addition of ferrous sulphate the bead assumes in the reducing flame the peculiar red colour of venous blood, whilst in the oxidising flame the light-brown colour of ferric oxide can be obtained at pleasure. The titanium compounds form with soda a bead which at first effervesces, and is colourless and transparent while hot, but becomes opaque on cooling. If to the hot bead stannous chloride be added, and if it then be heated in the lower reducing flame, a grey mass is formed, which dissolves on heating in hydrochloric acid, yielding a pale-amethystine-coloured solution.

27 & 28. *Tantalum and Niobium compounds* exhibit the same reactions as titanium.

29. *Silica compounds.—a.* Treated with soda in the oxidising flame, the silicates dissolve with more or less effervescence. The mass treated whilst hot with stannous chloride and fused does not yield a trace of blue colour on solution in warm hydrochloric acid; and the silicates may thus be distinguished from the compounds of titanic, tantalic, or niobic acids. The blood-red colour obtained with ferric oxide from these acids is also not yielded by silicates. Gelatinous silica separates out when the fused mass is carefully treated with water and acetic acid on the lamp-plate. Fine particles of any silicate yield, on fusion in a bead of microcosmic salt, a mass of gelatinous silica when fused, which on cooling forms a solid opaque mass swimming in the transparent bead.

30. *Chromium compounds.—a.* In *the spiral of platinum wire with soda* the chromium compounds give, when fused with repeated additions of nitre, a yellow mass, which, when pulverised on the plate and treated with water, yields a light yellow solution exhibiting the well-known reactions of chromic acid.

31. *Vanadium compounds* (*a*) treated with nitre and soda in the platinum spiral

yield a bright yellow mass, the solution of which, on addition of silver nitrate and acidification with acetic acid, yields a yellow precipitate. The fused mass when evaporated with aqua regia gives a yellow instead of a green solution, which becomes blue on addition of stannous chloride. If the mass contains much vanadium, the solution gives a yellowish-brown colour or precipitate on addition of an excess of cold concentrated hydrochloric acid.

32. *Manganese compounds* give an amethystine-coloured bead in the oxidising, and a colourless bead in the reducing flame; with soda and a little nitre, a green bead, the green aqueous solution of which turns red on addition of acetic acid, and then often becomes colourless, with separation of brown flocculi.

33. *Uranium compounds* give in the oxidising flame a yellow bead, which becomes green in the reducing flame, especially on addition of stannous chloride. These colours closely resemble those of the iron compounds, but may easily be distinguished, at least if no other colouring metallic oxide is present, by the fact that the uranium bead, when incandescent, emits a bluish-green light analogous to that which the uranium compounds exhibit when fluorescing. Beads of lead-oxide, stannic oxide, and a few other substances exhibit a similar phenomenon when incandescent, but they none of them yield, like the uranium compounds, a coloured bead on cooling. Insoluble uranium compounds may be decomposed by gentle heating on the platinum spiral with acid potassium sulphate. On powdering the melted substance with a few particles of sodium carbonate, absorbing the moistened mass with filter-paper, and adding a drop of potassium ferrocyanide, a brown spot is formed.

34. *Phosphorus compounds.*—The presence of phosphorus may easily be detected, even when mixed with large quantities of other substances, as follows:—The sample having been ignited, is rubbed fine on the porcelain plate, and introduced into a small glass tube of the thickness of a straw; into this tube, which is closed at the bottom, a piece of magnesium wire, about one-fourth of an inch in length, is placed so that it is covered by the powder. On heating the tube, magnesium-phosphide is formed with incandescence. The black contents of the tube powdered on the plate give, on moistening with water, the highly characteristic smell of phosphuretted hydrogen. A piece of sodium can be equally well used if magnesium cannot be procured. If it has been ascertained that the sample does not yield any film on porcelain in the upper oxidising flame, the phosphates may be recognised by heating on platinum with borax and a thin piece of iron wire in the hottest part of the reducing flame, when a bright molten bead of iron-phosphide is obtained which can be extracted with the magnetised knife on crushing the bead under paper.

35. *Sulphur compounds* give with soda on the charcoal splinter a fused mass, which leaves a black stain when brought on to moistened silver. As selenium and tellurium give rise to the same reaction, the absence of these substances must first be ascertained by seeing that no film of selenium or tellurium is deposited on porcelain. In the case of metallic sulphides, and not of sulphates, the simple ignition of the sample in the flame is sufficient to produce the peculiar smell of burning sulphur.

The following examples are given to illustrate the value of these methods in analysis:—

1. *A mixture of the Sulphides of Arsenic, Antimony, and Tin.*—If in a mixture of these three sulphides containing only traces of antimony and tin, they are separated according to the ordinary rules of qualitative analysis, by dissolving in alkaline sulphides and reprecipitation with acids, the detection of these two metals by the regular tests is extremely uncertain and troublesome. By the following method, however, their detection is rendered easy and certain when the proportion of tin is only a few thousandths, and that of the antimony only a few hundredths, of the total weight of the mixture.

Three decigrammes of the sulphides are roasted on a curved piece of glass, small enough to be altogether surrounded by the flame, and the residue, weighing only a few milligrammes, is scraped together with a knife. The moistened mass is then collected on the end of a thread of asbestos, and a strong metallic film obtained on the test-tube (see p. 132). In order to prevent the deposition of any carbon with the metals, which would act injuriously in the subsequent operations, the upper reducing flame is made so small that the luminous point is only just visible. The film is next dissolved in a drop or two of nitric acid, and the solution is evaporated below its boiling-point by gently warming and blowing, so as to obtain the solid residue in as small a space as possible. A drop of neutral silver solution is now brought on to the residue at the moment when it becomes solid; and on blowing with ammoniacal air, a characteristic black stain is formed, whilst the reaction of arsenic is also generally noticed. In

Table of Volatile Elements which

	Metallic film.	Oxide-film.	Oxide-film with stannous chloride.	Oxide-film with stannous chloride and soda.	Oxide-film with silver-nitrate and ammonia.
Te	Black; thin part brown.	White.	Black.	Black.	Yellowish white.
Se	Cherry-red; thin part brick-red.	White.	Brick-red.	Black.	White.
Sb	Black; thin part brown.	White.	White.	White.	Black; insoluble in ammonia.
As	Black; thin part brown.	White.	White.	White.	Lemon-yellow or reddish brown; soluble in ammonia.
Bi	Black; thin part brown.	Yellowish white.	White.	Black.	White.
Hg	Grey non-coherent thin film.				
Tl	Black; thin part brown.	White.	White.	White.	White.
Pb	Black; thin part brown.	Yellow-ochre colour.	White.	White.	White.
Cd	Black; thin part brown.	Blackish brown; thin part white.	White.	White.	White; in the thin parts turns bluish black.
Zn	Black; thin part brown.	White.	White.	White.	White.
Sn	Black; thin part brown.	Yellowish white.	White.	White.	White.

can be reduced as Films.

Iodide-film.	Iodide-film with ammonia.	Sulphide-film.	Sulphide-film with ammonium-sulphide.	
Brown; disappears for a time on breathing.	Disappears altogether on blowing.	Black to blackish brown.	Disappears for a time.	Elements whose reduction-films are scarcely dissolved in dilute nitric acid.
Brown; does not wholly disappear on breathing.	Does not disappear on blowing.	Yellow to orange.	Orange, and then disappears for a time.	
Orange-red to yellow; disappears on breathing.	Disappears altogether on blowing.	Orange.	Disappears for a time.	
Orange-yellow; disappears for a time on breathing.	Disappears altogether on blowing.	Lemon-coloured.	Does not disappear.	
Bluish-brown; thin parts pink; disappears for a time on breathing.	Pink to orange; chestnut-coloured when blowing.	Burnt-umber-colour to coffee-coloured.	Does not disappear.	Elements whose reduction-films are with difficulty dissolved in dilute nitric acid.
Carmine-coloured and lemon-yellow; does not disappear on breathing.	Disappears for a time on blowing.	Black.	Does not disappear.	
Lemon-yellow; does not disappear on breathing.	Does not disappear on blowing.	Black; thin parts bluish grey.	Does not disappear.	
Orange-yellow to lemon-colour; does not disappear on breathing.	Disappears for a time on blowing.	Brownish red to black.	Does not disappear.	Elements whose reduction-films are instantly dissolved in dilute nitric acid.
White.	White.	Lemon-coloured.	Does not disappear.	
White.	White.	White.	Does not disappear.	
Yellowish white.	Yellowish white.	White.	Does not disappear.	

order to detect tin, a few scarcely visible particles of the roasted sulphides are fused on a borax bead which has been very slightly tinted with cupric oxide. If the bead is now brought into the lower reducing flame, it assumes a ruby-red colour from reduced cuprous oxide. If the oxide be present in too large a quantity, the bead can be obtained transparent by the process described under the reactions of the copper compounds. This reaction can be obtained only in the lower reducing flame of the non-luminous gas-lamp, as in the ordinary blowpipe-flame the cupric oxide is reduced to cuprous oxide without the presence of tin-salt.

2. *Black Tellurium, containing Tellurium, Selenium, Antimony, Lead, Gold, and Sulphur.*—After the sulphur has been detected by the smell on roasting, the metallic film is obtained on a test-tube, which is then placed inside a wider and shorter tube containing a few drops of *concentrated* sulphuric acid, so that the metallic film is surrounded by the acid. If the temperature be now gradually raised, the presence of tellurium is at once ascertained by the formation of a bright carmine-colour. If the temperature be still further raised, the tellurium oxidises, and the olive-green colour of selenium becomes visible; the cooled solution, on dilution with water, then no longer exhibits the black precipitate of tellurium, but is coloured yellowish red from the selenium. If this substance is present in small traces only, it can be best detected by looking down the length of the test-tube upon a sheet of white paper. As common commercial sulphuric acid not unfrequently contains traces of selenium, it is well to make a blank experiment to assure one's self of its absence. The antimony is detected exactly as described in the preceding example. To detect the lead and gold, a sample is reduced on the charcoal splinter, the beads of the alloy are washed into a curved glass, and the flattened and dried metallic particles treated with pretty strong nitric acid as long as anything dissolves. The acid is then evaporated off, and the soluble portion of the residue dissolved in a drop or two of water. The solution is then brought on to a second curved glass by means of a capillary pipette, and the characteristic precipitate of lead sulphate obtained by addition of a few milligrammes of sulphuric acid. The gold, left undissolved as a brown powder, is completely washed by frequent addition of water and removal of the same with the capillary pipette. A portion of the dried particles of gold fused on a charcoal splinter with soda, yields in the mortar bright golden yellow particles, which may be dissolved in aqua regia and tested with stannous chloride.

ANALYSIS OF GASES. Williamson a. Russell (*Chem. Soc. J.* [2] ii. 238) have described a modification of their apparatus for gas-analysis (i. 274), in which the gases are subjected to the action of reagents in a 'laboratory-vessel' separate from the eudiometer, as in the apparatus devised by Regnault and by Frankland a. Ward (i. 276). This addition permits the use of liquid reagents, which act much more quickly than the solid absorbents used in the former apparatus and in Bunsen's original method. The transference of the gas between the eudiometer and the laboratory-vessel is, however, effected by an arrangement free from the fragility and liability to leakage which constitute the chief inconveniences attending the use of Regnault's and of Frankland a. Ward's apparatus. The eudiometer tube is surrounded by a cylinder of water, as in the apparatus just mentioned. For the detailed description of the apparatus and the mode of using it, we must refer to the original memoir, as it scarcely admits of abbreviation.

Russell (*Chem. Soc. J.* [2] vi. 128) has lately contrived a simpler form of apparatus, which permits the use of liquid reagents in the eudiometer itself, and thus does away with the complication of the laboratory-tube. This apparatus is represented in the following diagrams. The mercury-trough is made of gutta-percha; the form of it is shown in figs. 5 and 6. Fig. 5 is a horizontal section, and fig. 6 a section through A B. The larger part of the trough is circular; in this part stands the glass cylinder which contains the water, and in the centre are the eudiometer and pressure-tube. The form of the well in which these tubes are raised or lowered is represented at C; it is 2½ inches long, 1⅛ broad. The well for the pressure-tube is 14 inches deep measured from the bottom of the trough, and that for the eudiometer 19 inches. These are shown in fig. 6, E and F. The sides of the trough are 3½ inches high. The smaller part of the trough which is without the glass cylinder is shown in fig. 5. Along the bottom of this part there is a channel ⅝ inch wide, which runs into the well. The depth of this channel starting from the end of the bottom of the trough at B gradually increases till it reaches the well, where it is 1¾ inch deep: G H, fig. 6. The circular part of the trough is 3⅝ inches in diameter, and the total length through A B 6⅛ inches. The above dimensions are all inside measurements. The thickness of the gutta-percha is half an inch.

The pressure-tube is simply a straight piece of tubing of about the same diameter as the eudiometer. Fig. 7 represents the whole apparatus. The glass cylinder is omitted for the sake of clearness, also the eudiometer, but the clamp intended to hold it is shown in the figure.

The liquid reagent is introduced into the eudiometer by means of a small syringe, readily made from a piece of tubing about 8 or 9 inches long, and ⅛th inch internal diameter; one end of it is bent round so as to give it the form of a hook, and drawn out; into the other end a piston fits, made from a piece of stout steel wire, one end of it being roughened or a screw turned on it; and round this cotton wool is tightly wrapped till it just fits the tube. In order to have a measure of the quantity of liquid to be introduced into the eudiometer, it is convenient to make five or six marks on the straight end of the syringe with a file, a quarter of an inch apart. When the liquid is to be introduced, a dot with a piece of chalk is made on the piston, and it is then pushed down till this chalk dot reaches the mark corresponding to the volume of liquid to be injected.

Fig. 5.

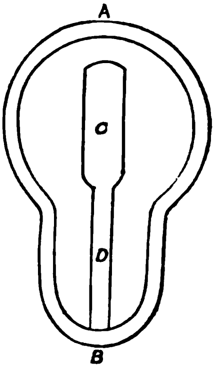


Fig. 6.

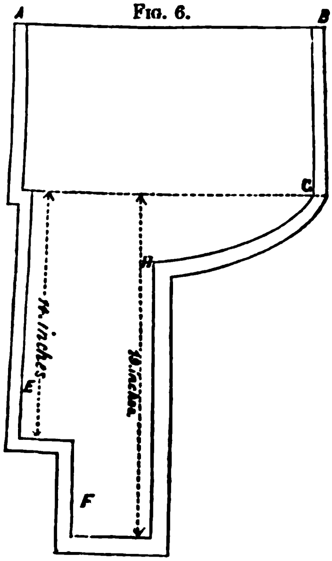
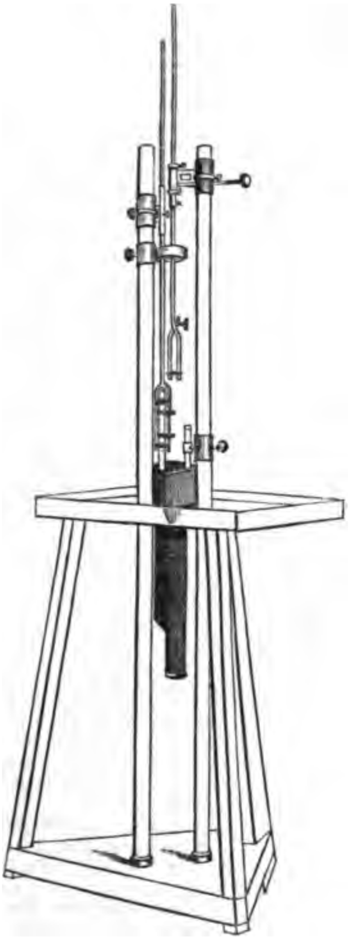


Fig. 7.



The next thing to be done is to remove this liquid reagent without altering the bulk of gas in the eudiometer. For this purpose, it is necessary to find some body which can absorb a certain amount of liquid, but will not carry air with it when introduced into the eudiometer, or abstract gas on being withdrawn. Wet cotton wool is found to have the required properties. It is used in this way: a piece of steel wire, size No. 9 or 10, has one end bent into a loop, and some cotton wool is twisted tightly round it; this mass of wool should be about ⅛ inch in diameter and ¾ inch long. It is placed in a basin of water, and thoroughly kneaded and squeezed for some time; this treatment wets the whole mass of cotton wool and expels all the air adhering to it.

This ball of cotton on the steel wire might of course be introduced into the eudiometer in the same way as Bunsen introduces his solid reagents; but it is found much more convenient, especially where it is important to have the mercury-trough small, to use what may be called a guide-tube. This is merely a piece of fine glass tubing about 8 or 9 inches in length, and bent into a curve at one end. The steel wire is introduced at this end and pulled through till the cotton ball prevents its going further. Held in this way the ball is easily introduced or withdrawn from the eudiometer, and that without dipping the fingers into the mercury. The ball being now held in the tube and thoroughly saturated with water, is lifted from the basin and plunged below the surface of the mercury in the trough; it is then squeezed between the finger and thumb, so as to expel a considerable portion of water, but still to leave it very wet. The guide tube is now introduced into the canal D, fig. 5, of the trough, and pushed down it so that the curved end with the ball comes within the tall glass cylinder. In order to introduce the ball into the eudiometer, the eudiometer is raised so that the open end of it is a little above the well in the trough; a mark on the cylinder, or on one of the supports, will indicate the point to which the top of the eudiometer must be raised in order that the open end of it may be in the right position. When it is thus raised, it is easy to hook the cotton ball projecting from the guide-tube into the eudiometer; then on pushing the wire, the ball rises in the tube and is completely under control. It is well to apply a very little grease to the wire, and if by any chance it should become bent, it must of course be discarded. To withdraw the reagent, the eudiometer is raised and the cotton ball introduced as above described; it is pushed up till the top of it comes in contact with the reagent, which is then quickly taken up by the cotton wool and the meniscus left free from liquid. The ball is now pulled below the surface of the mercury: this should be done with a jerk, to prevent any gas adhering to it, and withdrawn from the trough. The other manipulations with this apparatus are the same as with that of Williamson and Russell, described in vol. i. p. 274.

Russell has also described a method of accurately determining, by means of the apparatus just described, the volume of gas given off in any chemical reaction, and consequently of applying such measurements to various cases of quantitative analysis, such as the analysis of carbonates, the valuation of manganese peroxide and certain other oxides, by treatment with a mixture of sulphuric and oxalic acids, &c.

The measuring tube used in these determinations is about 29 inches long, and rather more than three-quarters of an inch in internal diameter. It is bent at right angles near the upper end, which is left open, and connected by a caoutchouc tube with a small flask, into which the reacting substances are introduced. The connection between the tube and the flask can be closed at pleasure by pressing the flexible tube with a spring clamp. The difference between the volume of air in the tube and flask before and after the reaction, gives, after proper correction, the quantity of gas produced. For details of manipulation we must refer to the original memoir (*Chem. Soc. J.* [2] vi. 310).

Another apparatus for quantitative analysis by measurement of the gases evolved in reactions, 'Gas-volumetrische Analyse,' chiefly in agricultural and techno-chemical investigations, is described by Fr. Schulze (*Zeitschr. anal. Chem.* ii. 289; *Jahresb.* 1863, p. 661).

Apparatus for measuring the gases absorbed in water, and given off on mixing with alcohol and heating, are described by Bobierre (*Compt. rend.* lvi. 313; and Robinet, *Ann. Ch. Phys.* [3] lxviii. 177; *Jahresb.* 1863, p. 665).

ANALYSIS, ORGANIC. Cloez (*Ann. Ch. Phys.* [3] lxviii. 394) describes an apparatus for the analysis of organic bodies, differing from that in general use chiefly by the substitution of iron combustion-tubes for those of glass. The iron tube, 1·15 metre long and 0·020 to 0·222 in diameter, is lined throughout with a layer of oxide by heating it to redness and passing steam through it, and is laid in a furnace of such a length that about 0·2 metre of the tube projects at each end. In the middle part of the tube is placed granulated cupric oxide, kept in its place by copper foil; and into each end is inserted a semi-cylindrical tray of iron plate, attached to a wire for drawing it out. The tray at the anterior end, which is 0·2 metre long, serves for the reception of various substances, according to the nature of the body to be analysed; thus, for azotised bodies, it is filled with metallic copper; for substances containing chlorine or sulphur, with lead chromate; for difficultly combustible substances, with cupric oxide; in other cases it is dispensed with. The posterior tray, 0·3 metre long, is filled to three-fourths with cupric oxide or lead chromate. The tube thus fitted up is heated to redness; a slow stream of dry air is passed through it so as completely to desiccate its contents; and the cupric oxide in the hinder tray (after cooling, either in the tube itself, or in a separate arrangement) is quickly mixed in an iron capsule with the substance to be analysed. The front end of the tube is next connected by corks with the apparatus for absorbing water and carbonic acid; the tray containing the substance is put into its place, and the combustion is completed as usual, a slow stream of air, previously freed with the utmost care from water and carbonic acid, being passed through the tube during the whole of the combustion. The end of the combustion is ascertained by comparing the numbers of air-bubbles which enter and leave the potash-bulbs. The same apparatus, with a particular arrangement for passing carbonic acid through the tube, may serve also for the estimation of nitrogen.

A method of organic analysis founded on gas-measurements, and resembling that originally employed by Gay-Lussac and Thénard (i. 226), is described by Fr. Schulze (*Zeitschr. anal. Chem.* v. 289; *Bull. Soc. Chim.* [2] viii. 263). The organic substance (weighing at most 0·010 to 0·012 grm.), mixed with a known weight of *potassium chlorate*, is burnt at a low red heat in a vacuous combustion-tube, and the gaseous products of the combustion are transferred to a eudiometer and analysed, the entire volume being first measured, and the carbon dioxide then determined by absorption. The carbon dioxide occupies the same volume as the oxygen contained in it; consequently after the combustion of carbohydrates ($C^nH^{2m}O^m$) with potassium chlorate the volume of oxygen in the eudiometer corresponds exactly to the oxygen contained in the chlorate; if the measured volume of gas is larger than this, the organic substance must have contained a quantity of oxygen larger than that required to burn the hydrogen contained in it; if smaller, the substance analysed must be richer in hydrogen than a carbohydrate.

Ladenburg (*Ann. Ch. Pharm.* cxxxv. 1) has described a method of organic analysis in which, as in the method of Gay-Lussac and Thénard, the carbon is estimated directly by the quantity of carbon dioxide produced, and the total quantity of oxygen consumed in the combustion is likewise determined, so that the difference between this and the quantity required for the combustion of the carbon gives the quantity which has combined with hydrogen, whence also the amount of the hydrogen itself may be calculated. The oxidising agent is a mixture of *silver iodate* with strong sulphuric acid. This mixture, when heated alone, even to 300°, does not give off either iodine or oxygen; but when it is heated in contact with an organic substance, carbon dioxide and water are formed by reduction of the iodic acid, whilst the hydriodic acid formed at the same time, together with free iodine, reacts on the iodic acid, necessarily present in large excess as silver salt, in such a mannner as to produce iodine and water (without formation of sulphurous acid):

$$IHO^3 + 5HI = 3I^2 + 3H^2O.$$

The process is as follows:—The substance to be analysed is weighed in a small glass bulb, which is introduced, together with concentrated sulphuric acid and a known quantity (excess) of silver iodate, into a strong glass tube, which is drawn out and sealed. The bulb having been broken by a slight blow, the tube is heated for an hour or two in an air-bath to 170°–200°, and weighed after cooling. The tube is then opened by heating its apex to redness, and the carbon dioxide resulting from the reaction is completely removed by warming the tube to 60° at most, then exhausting with a syringe, and passing a stream of dry air through it. On again weighing the tube the loss of weight gives the amount of carbon dioxide. The tube is then cut into small pieces, and the contents, having been carefully rinsed out, are digested with water in a closed flask, till the blackish colour of the precipitate (arising from a little free iodine) has passed into a yellowish-white. The mixture of silver iodide and iodate, having been thoroughly washed by repeated decantation with water, is dissolved in potassium iodide, and the liberated iodine is determined volumetrically in the dilute liquid by means of sulphurous acid, starch, and normal solution of iodine, after the wash-water of the silver salt diluted with sulphurous acid (and containing a little iodic acid) has been added to it. From the quantity of iodine thus determined, the weight of silver iodate still present is calculated, and thence also the amount which has been reduced; and this finally gives the quantity of oxygen which has been consumed in the oxidation of the substance. Lastly, the equation

$$9h = s + D - A,$$

in which s denotes the weight of substance burned, D the oxygen consumed, and A the carbon dioxide produced, gives the quantity h of the hydrogen.

C. G. Wheeler (*Sill. Am. J.* [2] xli. 33) has described a process for the simultaneous determination of nitrogen, carbon, and hydrogen, consisting essentially of a combination of the process of ultimate analysis in a current of oxygen with Maxwell Simpson's method of estimating nitrogen (i. 243). The combustion-tube, from 2 to 2½ feet long, is filled with the following substances:—1. A mixture of potassium chlorate and cupric oxide.—2. A layer of pure cupric oxide.—3. A mixture of cupric oxide with an exactly weighed quantity (about 0·5 grm.) of pure lead oxalate.—4. Pure cupric oxide.—5. The mixture of the organic substance with cupric oxide.—6. Pure cupric oxide.—7. Metallic copper. The combustion-tube is connected in the usual manner with a calcium chloride tube and a potash apparatus (terminating in a tube which contains solid potash), and the latter with a Bunsen's mercurial gasometer (ii. 808). The process is commenced by heating the potassium chlorate before connecting the apparatus with the gasometer, so as to replace the air by oxygen; the oxygen is then expelled by heating the lead oxalate, which evolves carbon dioxide, and then the metallic copper is heated, the gas-delivery tube being at the same time connected with the gasometer. The combustion is then carried on in the usual way, and when it is completed, oxygen is again evolved by heating the rest of the potassium chlorate. The nitrogen in the gaseous mixture collected in the gasometer is then determined eudiometrically. The quantity of carbon dioxide evolved from the lead oxalate is of course deducted from the weight of the potash apparatus after combustion. A series of experiments made with all sorts of nitrogen compounds for the purpose of testing this process gave very exact results.

Baumhauer (*Archives néerlandaises*, i. 179; *Zeitschr. anal. Chem.* v. 141) has perfected the apparatus formerly described by him (i. 239) for the simultaneous determination of carbon, hydrogen, and oxygen, as follows:—A combustion-tube 70 to 80 centim. long and open at both ends is filled with the following substances, beginning from the anterior extremity: 1. A layer of copper-turnings 20 centim. long.—2. A layer 20 centim. long of fragments of porcelain previously washed with hydrochloric acid and ignited.—3. A layer 25 centim. long of strongly ignited coarse-grained cupric oxide (between plugs of asbestos).—4. The substance to be analysed, contained in a boat of porcelain or platinum, or, in the case of volatile substances, in a glass bulb, which is pushed into the tube by means of a glass rod, to within 5 centim. of the cupric oxide; difficultly combustible substances are previously mixed in the boat with the cupric oxide.—5. At a distance of 6 or 7 centim. behind the substance is placed a second boat, containing a weighed quantity (a few grms.) of silver iodate. The posterior end of the combustion-tube (containing the silver iodate) communicates—by means of a tube containing ignited copper-turnings, a U-tube filled with pumice-stone soaked in sulphuric acid, and a second U-tube containing calcium chloride and soda-lime—with two gasometers, one containing pure nitrogen, the other hydrogen. Before attaching the apparatus for absorbing the water and carbon dioxide, the anterior part of the tube containing the copper-turnings is heated, and a slow stream of hydrogen is passed through it, till the surface of the metal is completely deoxidised. The hydrogen is then displaced by nitrogen, and the part of the tube containing the porcelain boat and the cupric oxide is heated in a continuous slow stream of the gas, the calcium chloride tube and the potash apparatus being at the same time attached. When the whole apparatus is filled with nitrogen, and the potash-ley is also saturated with that gas, the absorption apparatus are detached and weighed, then again attached, and the substance is carefully heated, the stream of gas being continually kept up. As soon as the organic substance is completely burned, or at least completely carbonised, the silver iodate is gradually heated, whereby the still remaining carbon is burned, and the copper reduced from the cupric oxide is reoxidised, the excess of oxygen being retained by the copper-turnings. After the complete decomposition of the silver iodate, the stream of nitrogen is kept up for some time, and then the absorption apparatus are weighed. In the next place, still without interrupting the stream of nitrogen, the copper-turnings alone are heated to redness (the fire being removed from the other parts of the tube), and when the cupric oxide is quite cold, a weighed calcium chloride tube is attached, and a stream of hydrogen is passed through the apparatus. The excess of oxygen of the silver iodate, which had been taken up by the copper-turnings, is thereby converted into water (*b*), and the weight of this water gives the quantity of oxygen contained in the silver iodate beyond that which was required for the complete combustion of the organic substance. If the boat be now removed from the combustion-tube, the latter is ready for another analysis.

As an example of the calculation and of the degree of exactness attained, we may take an analysis of oxalic acid.

Substances used: Oxalic acid 0·452 grm.; silver iodate 1·256 grm. (yielding on the average 16·92 per cent. oxygen), therefore 1·25 grm. yielding 0·2125 grm.

Quantities obtained.

Carbon-dioxide	0·443	containing	C 0·1208	and	O 0·3222
Water (*a*)	0·090	„	H 0·010	„	O 0·0800
Water (*b*)	0·1495	„		„	O 0·1330
					0·5352
Deduct for O from $IAgO^3$					0·2125
Remains for O from the oxalic acid . .					0·3227

Hence in 100 parts

	Carbon.	Hydrogen.	Oxygen.	Total.
Found . . .	26·73	2·21	71·39	100·33
Calculated $C^2H^2O^4$	26·66	2·23	71·11	100·00

For the simultaneous determination of nitrogen, there is attached to the potash apparatus a tube *a*, open above and below, and divided into centimetres: this is connected by a strong caoutchouc tube with a second glass tube *b*, of as nearly as possible the same dimensions. On pouring mercury through the latter, it is possible, by raising or depressing *b*, to bring the mercury in the tube into any required position. The whole being prepared for the analysis as in the former case, the tube *a* is connected with the potash apparatus, after it has been raised to such a height that *a* is completely filled with mercury. The supply of nitrogen gas is then cut off, and the tube *b* is depressed so far that the mercury in it stands about 200 mm. lower than in *a*; the whole is then left to cool, and the height of the mercury is observed, as well as the pressure and temperature. The mercury is then brought to the same level in *a* and *b*, and this level is read off. The combustion is now carried on in the manner above described, excepting that no nitrogen is passed through the tube, and, when the evolution of nitrogen from the substance has ceased, the apparatus is left to cool, the height of the mercury is read off, and in this way the amount of nitrogen is ascertained. The gas apparatus are then removed, and the combustion is terminated, as above described, by heating the silver iodate. Baumhauer recommends, however, that the nitrogen shall when possible be determined in a separate portion of the substance.

For Maumené's method of determining the oxygen in organic compounds, see *Zeitschr. anal. Chem.* i. 487.

According to Wanklyn a. Frank (*Phil. Mag.* [4] xxvi. 554), organic substances when ignited in a stream of hydrogen give up part (if not the whole) of their oxygen in the form of water, a reaction which affords a means of detecting the presence of oxygen in organic compounds.

A. Mitscherlich (*Pogg. Ann.* cxxx. 536; *Zeitschr. anal. Chem.* vi. 136) has devised a new method of organic analysis, which serves, amongst other purposes, for the direct estimation of oxygen. Two forms of process are employed, the combustion being made in a current of chlorine, or of oxygen, according to the elements to be determined.

1. When any organic substance is heated to redness in an atmosphere of *chlorine* free from oxygen, the hydrogen is wholly converted into hydrochloric acid, and may be estimated in that form, while the oxygen of the organic body unites with its carbon, or with charcoal added thereto, forming monoxide and dioxide of carbon, from the weight of which the oxygen in the organic substance may be calculated.

The combustion is performed in a porcelain tube 0·6 met. long and 9 mm. in internal diameter, half filled with charcoal. If the substance to be analysed is not volatile below 150°, it is enclosed in a glass tube open at both ends and introduced into the porcelain tube; if volatile below 150°, it is placed in a glass apparatus of peculiar construction. Gaseous substances are enclosed in a graduated jar immersed in water, and are passed into the combustion-tube by a tube attached laterally to that which conveys the chlorine.

The gases produced by the combustion are passed into absorption-bulbs of peculiar construction, called 'Mitscherlich's bulbs.' The hydrochloric acid resulting from the combustion of the hydrogen is absorbed by a concentrated solution of lead nitrate, which, according to the author, does not absorb free chlorine. The carbon dioxide is absorbed by potash. but it must be previously freed from chlorine by passing the gases through an alcoholic solution of stannous chloride or ferrous sulphate. The carbon monoxide is absorbed by passing it through a series of bulbs filled with a solution of cuprous chloride and hydrochloric acid.

2. For the determination of carbon, sulphur, the halogen elements, and nitrogen, the organic substance is heated in a current of hydrogen, and the mixture of hydrogen with the vaporised body, or its product of decomposition, is burnt in a current of oxygen. The combustion-tube is of hard glass, and is composed of a horizontal branch 200 mm. long, a downward bend of 130 mm., a second horizontal branch 250 mm. long, and a second bend directed upwards and drawn out to a narrow neck, to which the absorption-apparatus are attached. The lower horizontal branch is half filled with sulphuric acid, heated moderately towards the end of the process, to absorb the water generated in the combustion. This lower branch is divided into two parts by a curvature directed upwards. When the organic substance contains sulphur, the part next to the organic body is filled with a mixture of chloride and sulphite of calcium. The sulphuric acid, which is always formed, together with sulphurous acid, eliminates from this mixture an equivalent quantity of sulphurous acid. The oxygen which maintains the combustion is introduced by a lateral branch of the tube.

The carbon dioxide is absorbed by potash. There likewise remains in the tube containing the organic substance a residue which is regarded as pure carbon and is to be weighed as such. [Is it quite free from hydrogen?] The sulphurous acid is absorbed by a saturated solution of potassium chromate. Hydrochloric acid and bromine are absorbed by lead-nitrate contained in a bulb-apparatus to which is attached a tube, filled half with mercuric oxide and half with calcium chloride. Iodine is weighed in the free state in another tube. Nitrogen is collected at the end of the apparatus after being freed from the excess of oxygen by passing through a tube containing fragments of phosphorus.

Mitscherlich also describes a method of estimating hydrogen in a substance containing sulphur, viz. by volatilising it in a stream of carbon monoxide and burning it with excess of oxygen. The analyses made according to these methods yielded very exact results, but the processes are perhaps too complicated to supersede those in general use.

In a subsequent communication (*Deutsche Chem. Gesellschaft*, i. 45; *Bull. Soc. Chim.* [2] x. 378) Mitscherlich describes a simplified method, by which the carbon, hydrogen, and oxygen may be estimated in a single operation. In this method the chlorine is supplied by *potassium platinochloride*, a substance which gives up its chlorine when heated with organic bodies.

The substance to be analysed is introduced into a porcelain tube filled with a mixture of pumice-stone and potassium platinochloride (containing about 8 grms. of platinum); the air of the apparatus is expelled by a current of nitrogen gas; and the tube is heated to redness. Water is absorbed by phosphoric oxide, hydrochloric acid by lead nitrate, free chlorine by stannous chloride, and carbon dioxide by potash [is not carbon monoxide also sometimes formed?]; the products of the combustion still remaining in the tube are driven into the absorbing apparatus by a current of nitrogen; the whole is left to cool; and the absorption apparatus are weighed.

The porcelain tube is then again heated to redness, and a stream of oxygen is passed through it, whereby the remainder of the carbon is converted into carbon dioxide, which is absorbed in the same apparatus. To avoid any loss of carbon arising from the formation of a solid difficultly oxidable chloride, a glass tube containing cupric oxide is introduced into the porcelain tube, and the vapours of the chlorinated body are passed over this oxide, which burns the carbon completely.

Finally, there remains in the combustion-tube a mixture of pumice-stone, metallic platinum, and potassium chloride; and the tube may be rendered fit for a fresh analysis by passing a current of chlorine through it.

Very volatile substances and gases are introduced into the tube in the manner described in connection with the earlier form of the process, by the aid of a stream of nitrogen.

Estimation of Nitrogen.—Frankland found some years ago (*Phil. Trans.* cxlvii. 63) that in estimating nitrogen by Dumas' method, a certain quantity of the nitrogen sometimes passes off as nitrogen dioxide, even when a considerable quantity of metallic copper is placed in the anterior part of the combustion-tube, so that it becomes necessary to estimate the volume of the dioxide by means of solution of ferrous sulphate, and to deduct half its volume from the observed amount of the mixed gases. But from experiments recently made by W. Thorp (*Chem. Soc.* [2] iv. 359) in Frankland's laboratory, it appears that when the metallic copper is heated to bright redness, and the gaseous products of combustion are passed over it at a moderate rate, the whole of the nitrogen is evolved in the free state; whereas if the copper is heated only to dull redness, or if the gases pass over it too quickly, part of the nitrogen will escape as dioxide. The presence of a large quantity of aqueous vapour appears to interfere with the complete reduction of the oxides of nitrogen, so that in the analysis of azotised bodies containing much hydrogen, part of the nitrogen may escape reduction, even under conditions otherwise the most favourable; but the proportion of the nitrogen which thus escapes reduction does not exceed 3·76 p. c.; and in an actual analysis, even if the substance burned contained 20 p. c. of nitrogen, the error would be only 0·75 p. c., which would not very materially affect the results.

As the metallic copper used in the analysis of azotised bodies becomes oxidised when the combustion is performed in a stream of oxygen, Stein recommends the use of silver in place of it, that metal having also the advantage of retaining any chlorine that the organic substance may contain. Recent experiments by E. Calberla have shown that the silver completely reduces the nitrogen dioxide to free nitrogen, and does not exert the slightest decomposing action on carbon dioxide (*Bull. Soc. Chim.* [2] x. 382).

J. T. Brown (*Chem. Soc. J.* [2] iii. 211) has given a table to facilitate the calculation of the results of nitrogen determinations by Dumas' method. It gives the values of the fraction $\frac{\cdot 0012562}{(1 + 0\cdot00367T)760}$ for all values of T from 0° to 30°, the numerator being the weight of a cubic centimetre of nitrogen at 0° and 760°. For example, to find the weight of 53 c.c. nitrogen at 15°, and under a pressure of 743·3 mm., we should have

$$0\cdot00000156665 \times 53 \times 743\cdot3 = 0\cdot061718 \text{ grm.}$$

Table for the calculation of $\frac{0\cdot0012562}{(1 + 0\cdot00367T)760}$.

T		T	
0°	0·00000165289	16°	0·00000156121
1	164685	17	155582
2	164085	18	155047
3	163489	19	154515
4	162898	20	153986
5	162311	21	153462
6	161728	22	152941
7	161149	23	152423
8	160574	24	151909
9	160004	25	151398
10	159438	26	150891
11	158875	27	150387
12	158317	28	149887
13	157762	29	149389
14	157211	30	148896
15	156665		

For the estimation of nitrogen in substances (manures, for example) of which at least 25 to 30 grms. may be used, Ch. Mène (*Zeitschr. anal. Chem.* vi. 461) uses an earthen retort filled with lumps of potassium hydrate, and provided with a safety-tube. The substance, moistened with strong soda-ley, is introduced into the retort in the form of small pellets, and the retort is heated to low redness, beginning at the upper part. The ammonia must be collected in hydrochloric acid and weighed as ammonium platinochloride, inasmuch as the empyreumatic products would interfere with the volumetric estimation.

Respecting Schloesing's method of determining the nitrogen of organic compounds in the same operation with the carbon and oxygen, see *Zeitschr. anal. Chem.* vii. 269; *Jahresb.* 1867, p. 859.

Analysis of Compounds containing **Chlorine** *or* **Bromine.**—Gorup-Besanez (*Zeitschr. anal. Chem.* i. 438) finds that in the combustion of brominated organic compounds by the ordinary method, the quantity of carbon may come out considerably too low (as much as 10 p. c.). This result he attributes to the formation of a fusible copper bromide, which envelops portions of unburnt carbon and protects them from oxidation. To ensure the perfect combustion of the carbon in such bodies, he recommends the following process. At the posterior end of the combustion-tube, which is drawn out to a long bayonet-point, is placed a layer of cupric oxide 3 inches long; then an asbestos plug; next follows a porcelain boat containing a mixture of the organic substance with ignited lead oxide, and separated by a second asbestos plug from the granulated cupric oxide with which the rest of the tube is nearly filled, the anterior extremity being however occupied as usual by a layer of lead chromate or copper-turnings. The anterior portions of cupric oxide are heated first, then the posterior portions; afterwards heat is applied very gradually and carefully to the boat; and when the dry distillation is finished the combustion is completed in a stream of oxygen, care being taken not to heat the boat too strongly or to continue the stream of oxygen too long, as otherwise bromide of copper (or of lead) may be carried over into the calcium chloride tube.

Kraut (*Zeitschr. anal. Chem.* ii. 242) recommends that, in the analysis of organic compounds containing chlorine, bromine, or iodine, by means of cupric oxide and oxygen, a roll of silver leaf 5 inches long should be placed in front of the metallic copper. The silver will retain the whole of the chlorine, bromine, or iodine, even when oxygen is passed over it, and may be used many times before its surface requires to be renewed by reduction in a stream of hydrogen.

For the *detection* of iodine, bromine, or chlorine in organic compounds, Erlenmeyer (*Zeitschr. Ch. Pharm.* 1864, p. 638) decomposes a small quantity of the compound in a test-tube, the bottom of which is heated to low redness; the presence of either of these elements may then be recognised by the colour and reaction of its vapour. Liquid compounds may be conveniently examined for these elements by introducing a few drops of the liquid into the long neck of a glass bulb; on gently warming the bulb, and holding it with its neck directed downwards, the liquid is driven out, and may be directed on to the heated portion of the test-tube, where it will be decomposed.

For the *estimation* of chlorine (simultaneously with carbon and hydrogen), C. M. Warren (*Sill. Am. J.* [2] xlii. 156) places in the anterior part of the combustion-tube a mixture of cupric oxide (precipitated and ignited) with asbestos, to moderate the rapidity of the combustion. To prevent the volatilisation of cupric chloride, the part of the tube where this mixture is placed is heated to only 250°, in an air-bath of iron plate. When the combustion is completed, the cupric oxide is dissolved in dilute nitric acid, and the chlorine precipitated with silver nitrate.

In organic compounds containing a considerable proportion of hydrogen, the amount of chlorine, bromine, or iodine, may, according to Carius (*Ann. Ch. Pharm.* cxxxvi. 129), be very exactly determined by heating the compound with nitric acid and silver nitrate in a sealed tube (i. 247), in the manner described below in the case of sulphur compounds; but the chlorine compounds of the aromatic bodies, chlorobenzene for example, are but slowly and incompletely decomposed by this treatment. An exact estimation of chlorine in such compounds may however be obtained by heating them to about 200° with a mixture of potassium dichromate, silver nitrate, and nitric acid. The silver chromate usually mixed with the resulting silver chloride may be removed by diluting the contents of the tube with a considerable quantity of water and digesting with alcohol. In iodine compounds the resulting iodic acid must be reduced by sulphurous acid.

Estimation of **Sulphur** *and* **Phosphorus.**—Carius (*loc. cit.*) in 1860 described a method of estimating sulphur in organic compounds by heating them in sealed tubes with nitric acid (i. 247). This method he has now modified (*Ann. Ch. Pharm.* cxxxvi. 129) by using, instead of pure nitric acid (which often renders it necessary to evaporate the liquid after neutralisation with sodium carbonate, and fuse the residue), a mixture of nitric acid with potassium dichromate, in such proportion that the chromate—which, in oxidising the organic substance, forms potassium nitrate and chromic nitrate—shall be present only in slight excess. From 3 to 4 pts. nitric acid of sp. gr. 1·4 are sufficient for every 1 pt. of the required potassium chromate. The mode of conducting the process is as follows. From 0·15 to 0·40 grm. of the organic substance is sealed up together with the smallest possible quantity of air in a small glass bulb, the two ends of which are about a millimetre wide, very thin in the glass, and bent sideways. The bulb thus prepared is introduced into a tube of glass, 10 to 12 millim. wide, roundly sealed at one end, and about half filled with the mixture of nitric acid and potassium chromate. The glass tube is then drawn out at the upper end to a thick-walled capillary tube; the liquid is heated to the boiling point; and when all the air is expelled the capillary tube is sealed. After cooling, it is shaken till the ends of the bulb are so far broken as to form at each end an aperture about a millim. wide, by which the acid liquid can easily enter into the tube. The glass tube is then introduced into an iron tube, which is closed at one end, laid in an inclined position in an iron box serving as an air-bath, and heated therein by a gas-flame to 120°–140°. To open the tube at the end of the operation, it is left to cool completely; the liquid collected near the point is driven back by careful heating; and the extreme point is heated to redness, whereupon the gases escape quietly. The tube is then cut off below the narrow part, and the liquid containing all the non-gaseous products of the reaction is collected.

The resulting blue-green liquid is diluted with 8 or 10 volumes of water, and heated for an hour with 5 to 10 c.c. alcohol to reduce the chromic acid, after which the sulphuric acid is precipitated by barium chloride.

R. Otto (*Zeitschr. f. Chem.* [2] iii. 604) estimates sulphur in organic compounds by combustion with precipitated *cupric chromate*. The fore part of the tube must not be too strongly heated; the combustion should be made slowly; and the tube must be wide enough to prevent the cupric chromate from being driven out of it by the escaping gases. When the combustion is finished, the contents of the tube are digested with hydrochloric acid mixed with alcohol to reduce the chromic acid; the liquid is filtered; and the sulphuric acid contained in it is precipitated by barium chloride.

For the estimation of phosphorus in compounds which, like oxide of triethylphosphine, are not completely oxidised by nitric acid alone, Carius (*loc. cit.*) heats the substance to 180°, with a slight excess (about ⅛th more than is required for complete oxidation) of silver iodate and pure hydrogen sulphate (about 2 vol. to 1 vol. of the iodate). The contents of the tube are then diffused through cold water; the filtrate is heated with a little sulphurous acid; and in the liquid, again filtered and evaporated, the phosphoric acid is precipitated in the ordinary way as ammonio-magnesian phosphate.

Salts of Organic Acids.—For the analysis of the potassium, sodium, and barium salts of organic acids, the following process is recommended by Cloez (*Bull. Soc. Chim.* [2] i. 250). A known weight of the salt is mixed with at least 3 pts. of recently ignited *tungstic oxide*,* and the mixture is burned in a tared porcelain boat, by means of the previously described apparatus of Cloez for organic analysis with cupric oxide and a stream of air (p. 142). In this manner the carbon and hydrogen are determined as usual, and the increase in weight of the porcelain boat after the combustion gives at the same time the quantity of the base (as oxide). Trial experiments made with sodium acetate, potassium tartrate, and barium myristate yielded fairly accurate results.

For the more exact determination of the carbon in the alkaline salts of organic acids, C. Schaller (*Bull. Soc. Chim.* [2] ii. 93) mixes the salt with an equal weight of silica, and then with cupric oxide. Antimonic oxide was long ago recommended for the same purpose by Dumas a. Piria. Schaller estimates the amount of alkali in the salts of organic acids by igniting the salt with half its weight of silica, and weighing the residual alkaline silicate.

Mercury-compounds.—For the analysis of organic mercury-compounds, and of other mercury salts, Frankland a. Duppa recommend the following process. The combustion is made with cupric oxide, air, and oxygen, in a tube which is drawn out in two places near the anterior extremity, bent in a U-shape to receive mercury and water, and then connected with a sulphuric acid tube and a potash-apparatus. When the combustion is finished, and air is being passed through the tube, the mercury collected in the drawn-out part is driven by heat into the U-tube; the latter is then melted off, and connected, instead of the potash-apparatus, with a second sulphuric acid tube; and the water is transferred to the first sulphuric acid tube by means of a vacuum formed by the air-pump. The separation of water from mercury by means of a stream of air at ordinary temperatures is tedious and inexact; and if heat is applied, a portion of the mercury is always driven over into the sulphuric acid tube.

Proximate Analysis of Organic compounds by Limited Oxidation. Chapman a. Thorp (*Chem. Soc. J.* [2] iv. 477) have shown that the products formed by a regulated oxidation of organic compounds may yield important data for the determination of their molecular structure, and therefore for the investigation and characterisation of cases of isomerism. From experiments on bodies of the fatty series they conclude that complex organic molecules may be separated, by oxidation restrained within determinate limits, into molecules of simpler structure and much more difficult to oxidise, which may be regarded as the proximate constituents of the original more complex molecules.

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* Cloez prepares the tungstic oxide, (WO^3), by mixing the hot aqueous solutions of 100 pts. commercial crystallised sodium tungstate and 50 pts. sal-ammoniac, washing the separated ammonium tungstate with cold water, and igniting it in an open vessel.

The oxidising agents used consist of solutions of potassium dichromate mixed with the quantity of sulphuric acid required to produce acid potassium sulphate and chromic sulphate, and containing 3, 5, or 8 p. c. potassium dichromate. The substances to be oxidised are heated with these solutions in sealed tubes; the contents of the tubes are afterwards diluted with water and distilled; and the acid contained in the distillate is either immediately converted into a barium salt (for the saturation of the higher members of the fatty acid series, barium hydrate is better than the carbonate), or (to separate different acids that may be present) it is saturated with potash-ley, and the volatile acid is distilled off fractionally, after the successive addition of a quantity of titrated sulphuric acid sufficient to saturate one-third of the potash present (i. 250).

To remove all doubt as to the applicability of this method, Chapman a. Thorp have demonstrated, in the first instance, that acetic acid, propionic acid (prepared from ethyl-cyanide), valeric acid, and caproic acid (whether prepared from amyl cyanide or from the ketone obtained in the distillation of potassium ricinoleate), are not at all attacked, or only in traces (with formation of a small quantity of carbon dioxide), by subjection for twenty-four hours to the action of the 3, 5, or 8 p. c. chromic acid mixture at 100°; and consequently that these acids, when they occur as products of oxidation, remain unaltered in the mixture. At 130°, however, they undergo, more or less easily, a more thorough oxidation, which may be facilitated by the use of a larger excess of strong sulphuric acid, by the presence of free chromic acid, or of a small quantity of manganese dioxide, but never takes place if phosphoric acid is added instead of sulphuric. Dilute solutions of permanganic acid appear to act like the chromic acid mixture, inasmuch as they do not act on acetic or propionic acid even at the boiling heat (and but slowly on formic acid at ordinary temperatures in presence of sulphuric acid); concentrated solutions, however, decompose these acids with facility.

Those oxidation-products which are formed under the influence of a sufficient quantity of the oxidising mixture, and of exhaustive action, are designated as *proximate*; those obtained with an insufficient quantity of the oxidising agent, or when it is not allowed to act for a sufficient time, are called *mediate* products.

The results obtained with certain compounds by the above process, when the oxidation was normal and complete (the mixture of the substance with the chromic acid solution being usually heated to 80° or 90°, never above 100°), may be represented by the following equations:

Alcohols.

Ethyl Alcohol, $C^2H^6O + O^2 = C^2H^4O^2 + H^2O$
Amyl Alcohol, $C^5H^{12}O + O^2 = C^5H^{10}O^2 + H^2O$

Compound Ethers, obtained by the action of an Iodide on the corresponding Potassium-salt.

Ethyl Acetate, $C^2H^3(C^2H^5)O^2 + O^2 = 2C^2H^4O^2$*
Methyl Acetate, $C^2H^3(CH^3)O^2 + O^3 = C^2H^4O^2 + CO^2 + H^2O$†
Amyl Acetate, $C^2H^3(C^5H^{11})O^2 + O^2 = C^5H^{10}O^2 + C^2H^4O^2$‡
Amyl Valerate, $C^5H^9(C^5H^{11})O^2 + O^2 = 2C^5H^{10}O^2$‡
Amyl Nitrite, $C^5H^{11}NO^2 + O^2 = C^5H^{10}O^2 + HNO^2$
Ethyl Nitrate, $C^2H^5NO^3 + O^2 = C^2H^4O^2 + HNO^3$
Methyl Nitrate, $CH^3NO^3 + O^3 = CO^2 + HNO^3 + H^2O$

Iodides.

Ethyl Iodide, $2C^2H^5I + O^5 = 2C^2H^4O^2 + H^2O + I^2$
Amyl Iodide, $2C^5H^{11}I + O^5 = 2C^5H^{10}O^2 + H^2O + I^2$
Isopropyl Iodide, $2CH(CH^3)^2I + O^{11} = 2C^2H^4O^2 + 2CO^2 + 3H^2O + I^2$

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[*] The same products were likewise obtained with permanganic acid, both at ordinary and at higher temperatures.

[†] Formic acid in small quantity was detected in the distillate.

[‡] The oxidation takes place slowly, but completely, with a sufficient excess of the dilute (5 p. c.) chromic acid solution; with a very concentrated solution of chromic acid the oxidation goes further.

Amines.

Ethylamine, $C^2H^5.NH^2 + O^2 = C^2H^4O^2 + NH^3$
Propylamine, $C^3H^7.NH^2 + O^2 = C^3H^6O^2 + NH^3$
Amylamine, $C^5H^{11}.NH^2 + O^2 = C^5H^{10}O^2 + NH^3$*
Ethylamylamine, $C^5H^{11}.C^2H^5.NH + O^4 = C^5H^{10}O^2 + C^2H^4O^2 + NH^3$.

Hydrocarbons, C^nH^{2n}.

Ethylene, $C^2H^4 + O^6 = 2CO^2 + 2H^2O$†
Amylene, $C^5H^{10} + O^7 = 2C^2H^4O^2 + CO^2 + H^2O$‡
β Hexylene, $C^6H^{12} + O^7 = C^3H^6O^2 + C^2H^4O^2 + CO^2 + H^2O$‡.

From ethyl alcohol there were obtained, as intermediate products, aldehyde and ethyl acetate; from amyl alcohol, valeraldehyde and amyl valerate; from amyl acetate, valeraldehyde.

Mannite and glycerin, when heated with potassium hydrate, yield the same products as the hydrocarbons obtained by acting upon them with hydriodic acid and decomposing the resulting iodides with alcoholic potash. (Mannite yields propionic, acetic, and formic acids; glycerin yields acetic and formic acids.) It therefore appears remarkable that the chromic acid mixture oxidises both these bodies with violent reaction, to acetic and carbonic acids, and that mannite is decomposed by an acidulated solution of potassium permanganate at a gentle heat, according to the equation:

$$C^6H^{14}O^6 + O^7 = 6CH^2O^2 + H^2O.$$

Respecting the products of oxidation of the *diatomic hydrocarbons*, results different from those above detailed have been obtained by Truchot (*Compt. rend.* lxiii. 274). According to this chemist, ethylene and its homologues yield by oxidation with potassium permanganate, the fatty acid immediately lower in the series than the hydrocarbon itself. Thus when a solution of potassium permanganate is poured into a bottle filled with ethylene and standing in cold water (the solution containing 12 to 14 grms. of the crystallised salt to 1 litre of ethylene gas) the liquid is completely decolorised, and yields—after the manganic oxide has been removed by filtration, and the concentrated scarcely alkaline filtrate distilled with tartaric acid—nothing but formic acid with more or less carbon dioxide—no acetic acid. Propylene similarly treated is converted into formic and acetic acids; amylene yields acetic, propionic, and butyric, together with a small quantity of formic acid.

These results have to a certain extent been confirmed by Chapman a. Thorp. They find, however, that the higher acids are produced only when an alkaline oxidising agent is employed, and that even in this case they may be resolved by prolonged oxidation into carbonic and acetic acids. Hence they regard Truchot's results as relating only to imperfect oxidation, or perhaps as obtained by operating on mixtures of isomeric hydrocarbons.

The reactions above described are sufficiently exact for the quantitative estimation of the several groups of carbon-compounds into which a complex molecule is thereby resolved. For this application of the process of limited oxidation, which has been worked out by Chapman a. Smith (*Chem. Soc. J.* [2] v. 173; *Jahresb.* 1867, p. 338), it is sufficient to know—

1. The quantity of carbon dioxide produced.
2. That of the organic acids or neutral volatile bodies formed.
3. The quantity of oxygen required for the oxidation.

The methods adopted in these determinations are as follows:

1. *Carbon Dioxide.*—The substance to be oxidised (0·2 to 0·5 grm.) is introduced into a flask having a tube soldered laterally to its neck, whereby it is connected with a Will and Varrentrapp's bulb-apparatus (containing strong sulphuric acid for absorbing the vapours), and then with a potash-apparatus and potash-tube. Into the stopper of the flask is fixed a bulb-pipette provided with a stopcock and containing the required quantity of the chromic acid solution (100 grms. potassium dichromate and 126 grms. concentrated sulphuric acid in 1,000 c.c., 150 c.c. of this solution being

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* The oxidation succeeded best when the substance was first heated to 70°–80° for half an hour with concentrated chromic acid solution, and this mixture after dilution was heated in the water-bath.

† This compound was oxidised only by a concentrated solution of chromic acid; formic acid was not found among the products.

‡ The rapid evolution of carbon dioxide rendered it necessary to open the tube and close it again during the experiment.

sufficient for the purpose). The weight of the filled potash-apparatus having been determined, the chromic acid solution is allowed to run into the flask; the flask is heated in the water-bath after the pipette has been closed; and the evolution of carbon dioxide and the termination of the experiment are regulated as in a combustion analysis, the vessel containing the sulphuric acid being at the same time carefully kept cool. The carbon dioxide may also be estimated, though less conveniently, by loss.

2. *Volatile Acids or Neutral Compounds.*—The weighed substance is heated in a closed tube to 100° for about an hour and a half, with a 10 p. c. dichromate solution; the contents of the tube are emptied out into a flask, treated with zinc to reduce the chromic acid still present, and distilled several times to dryness, with repeated addition of water; the united distillates are saturated with barium carbonate; the solution is evaporated; and the weight of the barium salt dried at 150° is determined. The nature of the acid is indicated by the determination of the barium, and, after the separation of that element, by partial saturation and distillation. Neutral volatile substances insoluble in water and in saline solutions may be separated by distillation, receiving the distillate in potash-ley, and saturating it with carbonic acid.

3. To determine the *oxygen consumed*, the oxidised liquid is heated to boiling with excess of potash-ley; the precipitate of chromic oxide (which still retains potash, even after careful washing) is dried, ignited, boiled with strong sulphuric acid and a little alcohol, and again precipitated by ammonia.

As, however, the accuracy of this method is somewhat impaired by the uncertainty relating to the atomic weight of chromium, Chapman, in a subsequent communication (*Chem. Soc. J.* [2] v. 227), recommends the employment of a known weight of potassium dichromate, and the determination of the excess of chromic acid still remaining after the oxidation. Two equal portions of the dichromate solution are taken. One of them is decomposed directly with excess of oxalic acid and dilute sulphuric acid; and the carbon dioxide eliminated is estimated in the manner above described, the liquid being finally heated to the boiling point and kept there for a few seconds. (Percussive ebullition may be prevented by throwing in a few fragments of tobacco-pipe stems.)

A second portion of the solution is made to act upon a known weight of the organic substance, and the mixture is then treated in the same manner with oxalic acid and dilute sulphuric acid. The difference in the quantities of carbon dioxide in the two estimations corresponds to the oxygen consumed by the organic body, which oxygen (since the formation of 88 pts. carbon dioxide from oxalic acid requires 16 pts. oxygen) is calculated therefrom by multiplying by $\frac{2}{11}$.

The following examples may serve to exhibit the utility and scope of this method:

1. *Lactic acid* is oxidised by chromic acid in such a manner that $\frac{1}{3}$ of its carbon is converted into carbon dioxide, and the remaining $\frac{2}{3}$, first into aldehyde (on heating in the water-bath), then into acetic acid (on heating under pressure):

$$C^3H^6O^3 + O^2 = C^2H^4O^2 + CO^2 + H^2O.$$

Barium lactate gave 7·76 and 7·69 p. c. carbon as carbon dioxide, and 80·64 p. c. pure barium acetate:

	Found	Calc.
C in form of carboxyl (CHO^2)	7·72	7·62
C in the acetyl compound	15·21	15·24

2. *Diethoxalic acid*, $C^6H^{12}O^3$, is resolved by oxidation into carbon dioxide and propione, $C^5H^{10}O$:

$$C^6H^{12}O^3 + O = CO^2 + C^5H^{10}O + H^2O.$$

	Found	Calc.
C in form of carboxyl	9·093	9·091
Propione	65·7	65·15

3. *Propione* heated in a sealed tube with the oxidising liquid yields propionic and acetic acids:

$$C^5H^{10}O + O^3 = C^2H^4O^2 + C^3H^6O^2.$$

	Found	Calc.
100 pts. propionic consumed of oxygen .	57·83	55·8 pts.
and yielded barium acetate and propionate	310·5	312·8 „
The barium in this mixture amounted to .	50·94	50·93 p. c.

Diethoxalic acid contains therefore altogether, in accordance with the formula synthetically established by Frankland a. Duppa:

	Found	Calc.
C in form of carboxyl	9·09	9·09 p. c.
C in the propylic form	27·29	27·27
C in the ethylic form	18·20	18·18

The determination of the quantity of oxygen consumed in such reactions was found by Chapman, following the second method, to yield the following results:

I. For the conversion of butyric ether into butyric and acetic acids.—II. Of propione into propionic and acetic acids.—III. Of diethoxalic acid into carbon dioxide, propionic acid, and acetic acid: the organic substance being in each case heated in a sealed tube with a sulphuric acid solution containing 7 p. c. potassium dichromate:

	I.	II.	III.
Oxygen found . . .	27·71	55·90	48·66 p. c.
„ calculated. . .	27·58	55·81	48·48 „

Proximate Analysis of Vegetable Tissues (Frémy a. Terreil, *Bull. Soc. Chim.* [2] x. 437).—This branch of analysis presents peculiar difficulties, arising partly from the great similarity between the several proximate constituents of vegetable tissue, and secondly from the insolubility of these constituents in all the neutral liquids, such as water, alcohol, ether, &c., which are commonly used in proximate analysis. Frémy and Terreil, however, by the use of more powerful reagents, such as the mineral acids, alkalis, chlorine, &c., have succeeded in obtaining a more complete analysis of several vegetable tissues than any that have hitherto been made.

As an example, they give the analysis of oak-wood. This they find to consist of three parts, viz. (1) The *ligneous cuticle*, which is quite insoluble in hydrated sulphuric acid, $SO^3.2H^2O$ or $SO^4H^2.H^2O$, insoluble also in potash, but is dissolved by chlorine-water and nitric acid, after being first transformed into a yellow acid. This substance, which bears considerable resemblance to the cuticle of leaves, appears to form the cutaneous covering of the fibres and cells of the wood; when separated from the other constituents by means of sulphuric acid, it retains perfectly the structure of the ligneous tissue, so that when examined by the microscope it looks like the wood itself, of which however it forms only about one-fifth.—(2) The *incrusting matter* (Payen) which probably exists in the interior of the fibres and cells. It is soluble in sulphuric acid, which it blackens, but insoluble in chlorine-water. It is not however a definite substance, but a mixture of three others, one of which is soluble in boiling water, a second soluble in alkalis, and a third, which becomes soluble in potash, after being treated with chlorine.—(3) The *cellulosic substance*, which, when pure, dissolves without coloration in strong sulphuric acid, producing a liquid which is not precipitated by water; it is attacked with difficulty by chlorine-water and nitric acid.

Quantitative Analysis.—*α*. To determine the *cellulosic substance*, 1 grm. of sawdust dried at 130° is placed for 36 hours in a vessel filled with chlorine-water, which dissolves the ligneous cuticle and part of the incrusting matter, leaving the cellulosic substance mixed with another part of the incrusting matter, which is converted by the chlorine into an acid soluble in potash. Hence by treating the residue with an alkaline solution, washing it with acid, then with water, and drying at 130°, the cellulosic substance is obtained quite pure. In this manner it is found that oak-wood contains 40 p. c. and ash-wood 39 p. c. of cellulosic substance.—*β*. To determine the *ligneous cuticle*, 1 grm. of sawdust is treated for 36 hours with sulphuric acid of strength corresponding to the formula $SO^4H^2.3H^2O$ (or in some cases to $SO^4H^2.H^2O$), which completely dissolves the cellulosic and incrusting substances, while the cuticle remains suspended in the liquid. The residue is washed with pure water, and with alkaline water, and dried. Oak-wood is thus found to contain 40 p. c. of ligneous cuticle, ash-wood only 17 p. c.—*γ*. The *incrusting matter* is estimated by difference, and further decomposed as above described.

The total result in the case of oak-wood is as follows:

Ligneous cuticle . . .	20		
Cellulosic substance . .	40		
Incrusting matter . . .	40	Matter soluble in water. .	10
		Body soluble in alkalis . .	15
		Body transformed into an acid by moist chlorine . .	15

ANALYSIS, VOLUMETRIC. *Acidimetry* and *Alkalimetry*.—For the volumetric analysis of acids, Grandeau (*J. Pharm.* [3] xxxiv. 209) recommends the use of *pure calcium carbonate* in such a manner as to obviate the necessity of preparing a normal solution of potash or soda. A known volume (about 100 c.c.) of the acid to be tested is diluted to a litre; 2·5 grms. of pure dry calcium carbonate are introduced into a wide-necked flask; dilute acid is added by separate portions of

10 c.c. till the calcium carbonate is quite dissolved; and then a few drops of litmus tincture are added. In another flask, a volume of the same, and equal to that above employed, is also mixed with a few drops of litmus tincture, and the two liquids are saturated with dilute soda or potash-ley, the volumes of the alkaline liquid used for the purpose being noted. The difference of the volumes of the alkaline liquid added in the two cases contains a quantity of alkali equivalent to the calcium carbonate which has saturated a portion of the acid (the volume of which is therefore known), whence also the quantity of acid equivalent to the lime, and the entire quantity of acid, may be calculated.

Mohr (*Lehrbuch der Titrirmethode*) recommends the use of *oxalic acid*, $C^2H^2O^4.2H^2O$, for the preparation of a normal acid solution instead of sulphuric acid, because it is unalterable in the air, being neither deliquescent nor efflorescent; and may be obtained nearly pure in commerce, and completely purified by treating it with a quantity of water insufficient to dissolve it entirely, then filtering, crystallising, and draining the crystals. To prepare the standard solution, take $\frac{126}{2}$ = 63 grms. or 1 equivalent in grams of the crystallised acid; place it in a gauged litre bottle filled two-thirds with distilled water, giving the vessel a rotatory movement to facilitate the dissolution; and fill it up to the gauge-mark with distilled water. If the temperature of the air is 15°, each cubic centimetre will contain 0·063 grms. or $\frac{1}{1000}$ of an equivalent of the crystallised acid.

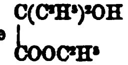
Pincus (*J. pr. Chem.* lxxvi. 171) recommends normal *nitric acid* titrated by means of calcium carbonate, nearly in the manner described by Grandeau. Pure dilute nitric acid and potash-ley (free from carbonic acid) are prepared of such strengths that equal volumes of the two saturate one another completely. A weighed quantity (about 1 grm.) of coarsely pulverised Iceland spar is then dissolved at a gentle heat in a measured quantity (in excess) of the acid (which has been made of equal value with the potash), and the excess of acid is then determined by titrating back again with the potash-ley. This gives the volume of acid equivalent to the dissolved lime, and thence it is easy to calculate how much water must be added to the original acid, as also to the potash-ley, in order that 1 cubic centimetre of it may correspond to $\frac{1}{1000}$ of an equivalent of any other acid or base. When the nitric acid has once been thus correctly titrated, and the potash-solution accordingly, it is easy, by means of the latter, to titrate sulphuric, oxalic, or any other acid with perfect accuracy.

Langer and Wawnikiewicz (*Ann. Ch. Pharm.* cxvii. 236) have tested a process, suggested by Bunsen, for applying the standard solutions commonly used for the titration of free acids and alkalis, to the estimation of all acids when in combination with bases which are separable completely and without contamination by caustic or carbonated alkalis. If the salt which is to be examined for its amount of acid be mixed with an excess of titrated alkali-solution till the base is completely precipitated, and the amount of alkali in the liquid filtered from the precipitate be then determined, the quantity of acid which was united with the base in the salt under examination may thence be found. A weighed quantity of the salt is dissolved in water, mixed with the titrated alkali, till a strong alkaline reaction is produced, and, after stirring, a definite volume is filtered off from the known total volume, and the filtrate is titrated for its amount of free alkali. At a proper degree of dilution, the uncertainty arising from the circumstance that the liquids do not occupy exactly the same volume before and after mixture falls within the limits of the other errors of observation. Experiments with various pure nitrates and sulphates gave very exact results. With some salts it was found necessary to heat the alkaline liquid; in the case of bismuth nitrate, exact results are obtained only when sodium carbonate is used, and the liquid supersaturated therewith is boiled for half an hour.

Wolcott Gibbs (*Sill. Am. J.* [2] xliv. 207) has generalised the method proposed by H. Rose for the estimation of nitric acid in certain nitrates, which consists in precipitating the metal by hydrogen sulphide and titrating the acid thus set free. All salts containing non-volatile acids and metals easily precipitable by hydrogen sulphide may be analysed in the same manner. The precipitation should be made at boiling heat, and when it is complete, the precipitate is washed on a filter, and a determinate quantity of the filtrate is titrated by means of a normal alkaline solution.

Titration of Compound Ethers.—Berthelot and Péan de St. Gilles (*Instit.* 1862, p. 110) test the purity of compound ethers by heating them in sealed tubes for 24 hours with a known volume (in excess) of standard baryta-water. The quantity of acid in the ether is then determined by titration of the excess of baryta with standard sulphuric acid.

Wanklyn (*Chem. Soc. J.* [2] v. 170) decomposes compound ethers with a standard solution of alcoholic potash, containing about 6 per cent. potassium hydrate, prepared by dissolving potash in pure alcohol of about 85 per cent. The digestion of the ether with the alcoholic potash is performed in a long-necked flask, and is for the most part accomplished with great ease and rapidity. The complete disappearance of the smell of the compound ether is in many cases a good criterion of the completion of the reaction. The quantity of acid in the ether is then determined as in Berthelot's method, by titrating the residual potash with standard sulphuric acid. This method gives very exact results, as the following experiments will show:

	100 pts. neutralise of potassium:		
	Exp.		Theory.
Ethyl Benzoate . . .	25·77	25·78	26·06
Ethyl Butyrate . . .	34·10	33·98	33·70
Ethyl Valerate . . .	30·15	30·77	30·08
Ethyl Diethoxalate  $\begin{array}{l}C(C^2H^5)^2OH\\ \vert\\ COOC^2H^5\end{array}$	24·20	——	24·44

Titration of Alkaloïds.—F. F. Mayer (*Rép. Chim. app.* v. 102) describes a process for the volumetric estimation of organic bases founded on their precipitability by potassio-mercuric iodide. The standard solution contains in the litre 13·546 grms. ($\frac{1}{10}$ eq.) mercuric chloride and 49·8 grms. potassium iodide; it is to be added to the solution to be tested (not the reverse), and yields distinct precipitates with various bases to the degrees of dilution shown in the following table:

Morphine . .	2,500	Narcotine . . .	50,000	Quinine . .	125,000
Atropine . . .	7,000	Brucine . . .		Strychnine .	150,000
Conine . . .	800	Quinidine . . .			
Nicotine . . .	25,000	Cinchonine . .	75,000		

The formation of the precipitates is hindered by the presence of alcohol, ammonia, or acetic acid, but not by extractive matters. For greater accuracy, the excess of the precipitant added should be determined by a normal silver solution.

Volumetric Analysis depending on Absorption of Oxygen.—Mittenzwey (*J. pr. Chem.* xci. 81) describes a process for the volumetric estimation of tannic acid, gallic acid, iron, manganese, and other substances, depending on the measurement of the quantity of oxygen absorbed by these substances in presence of alkalis. The vessel used for the purpose is a half-litre bottle, having a stopper of cork or caoutchouc, through which passes a glass tube bent towards the inner surface of the bottle. With this tube is connected, by a caoutchouc tube which can be closed by a spring clamp, a second glass tube, bent in the same direction as the first, and somewhat narrowed towards the end. In performing an analysis, the bottle, filled with 150 to 200 c.c. of the alkaline liquid and with renewed air, is shaken for a minute or two—avoiding all change of temperature—and the point of the outer tube is then immersed in water (contained in a beaker glass and standing at the same level as the liquid in the bottle), till on opening the spring clamp, no more water passes over into the bottle. The weight of water which thus passes over gives, with due regard to pressure and temperature, the volume of oxygen absorbed: 1 grm. of tannic acid or 0·7 grm. of gallic acid dissolved in 200 c.c. of 3 to 5 per cent. potash-ley (or of 2 to 3 per cent. soda-ley) absorbs 175 c.c. oxygen; with more concentrated solutions the absorption is less complete. Gallic acid absorbs oxygen much more rapidly than tannic acid. Iron and manganese compounds (for which latter, however, the particular oxide formed has not been determined) are introduced into the vessel in the forms of dissolved ferrous or manganous salt, together with a little solid caustic potash.

Volumetric Analysis without Weighing.—The problem proposed by Mohr (*Ann. Ch. Pharm.* cxvi. 128), 'To carry out analytical weight-determination, *without the use of weights*, with solutions of unknown strength, and the strength of which is moreover not to be determined,' has been solved by Pauli, Hillier, and Dietrich (*ibid.* cxvii. 386; *Jahresb.* 1860, p. 612). The general principle of the solution is as follows:

Equal quantities of the pure and impure substance to be titrated are weighed out, and measured volumetrically with the same liquid, any given number of cubic centimetres of which will of course give 100 per cent. for the pure substance, and a proportionally smaller quantity for the impure substance. The pure substance may also be replaced by another of similar chemical activity (e.g. manganese dioxide by potassium dichromate or iodine, sodium carbonate by calcium carbonate, &c.). It then only remains to compare by calculation the (known) quantitative difference of action exerted by the two substances to be titrated on the measuring liquid.

ANAMESITE. A variety of dolerite occurring at Steinheim, near Hanau, intermediate in character between crystalline dolerite and compact basalt. For analyses see *Jahresb.* 1865, p. 921; 1866, p. 973.

ANAMIDES. This name is applied by Baeyer (*Ann. Ch. Pharm. Suppl.* v. 79) to compounds derived from amides by abstraction of ammonia, just as anhydrides are formed from acids by abstraction of water; thus:

Orthocarbonic acid,	$C(HO)^4$	Carbotetramide,	$C(NH^2)^4$
First Anhydride,	$C(HO)^2O$	First Anamide (Guanidine),	$C(NH^2)^2NH$
Second Anhydride,	CO^2	Second Anamide (Cyanide),	$\begin{cases} C(NH)^2 \\ \text{or} \\ CN(NH^2) \end{cases}$

ANATASE. This form of titanic oxide has been found to occur in an oolitic iron ore from the coal-beds of Cleveland (Wöhler, *Jahresb.* 1867, p. 980).

ANCHIETINE. A substance obtained from the root-bark of *Anchieta salutaris*, and supposed to be the medicinal principle of that bark. It is extracted by leaving the crushed bark in contact with the air till it is completely fermented, then exhausting with hydrochloric acid, and precipitating with ammonia from the filtered solution. It crystallises in straw-yellow needles without odour, having a nauseous taste, insoluble in ether and in cold water, slightly soluble in boiling water, easily in alcohol, forming a slightly alkaline liquid. Dilute acids neutralise it, forming salts, some of which are crystallisable (Peckolt, *Arch. Pharm.* [2] xcvii. 271).

ANDESIN. This mineral is found accompanying the emeries of Chester County, Pennsylvania. Structure fine-grained. Fracture conchoïdal. Hardness = 7·5. Sp. gr. = 2·586. Colour, greenish-white. Contains 62·00 p. c. SiO^2, 24·40 Al^2O^3, 3·50 CaO, 0·70 MgO, 8·07 Na^2O, and 1·00 water (= 99·67) (F. Jackson, *Sill. Am. J.* [2] xlii. 107; *Bull. Soc. Chim.* [2] viii. 420).

ANDROPOGON. A genus of grasses, the leaves of which yield several fragrant volatile oils. Citronella oil, from the leaves of *A. Schœnanthus*, consists almost wholly of an oxygenated oil boiling at 200°, and having a sp. gr. of 0·8741 at 20°. Lemon-grass oil, from *A. Nardus*, has very nearly the same properties. Indian geranium oil (probably identical with East Indian grass oil, from *A. Iwarancusa*, ii. 942) contains several bodies scarcely separable by distillation. Respecting the optical properties of these oils, see Oils, Volatile, iv. 186.

ANEMONIN and **ANEMONIC ACID** are produced, according to O. L. Erdmann (*Jahresb.* 1858, p. 512), from the acrid liquid obtained by distillation of *Ranunculus sceleratus*. S. Dobraschinsky (*Jr. Pharm.* [4] i. 319) prepares anemonin by distilling the fresh flowering herb of *Anemone pratensis* with water, agitating the distillate with $\frac{1}{6}$th pt. of chloroform, and dissolving the residue of the chloroform extract in hot alcohol; the anemonin then separates in crystals.

ANETHOÏN. See the next article.

ANETHOL or **ANISE-CAMPHOR.** $C^{10}H^{12}O$.—Kraut and Schlun (*Zeitschr. Ch. Pharm.* 1863, p. 359; *Jahresb.* 1863, p. 551) have examined the liquid and solid modifications of anethol from oil of anise and oil of fennel, and have found that this body is optically inactive in both modifications, from whichever source it may be obtained; further, that anise and fennel oils are mixtures of liquid and solid anethol in various proportions, but that fennel oil likewise contains a hydrocarbon, $C^{10}H^{16}$, which turns the plane of polarisation to the right; anise-oil, which does not contain this hydrocarbon, is optically inactive. Solid anethol melts at 21·1°, boils at 232°, and has a sp. gr. of 0·989 at 28°. Anisoïn (i. 298), better called anethoïn, may be obtained by the action of stannic chloride or of strong sulphuric acid, either on solid or on liquid anethol, also from metanethol (most conveniently by distilling anise-oil with strong sulphuric acid). Anisoïn is resolved by dry distillation into liquid metanethol, which passes over, and a solid modification, *isanethol*, which remains behind.

Metanethol boils at 232·5°, has a sp. gr. of 0·9708 at 18°, may be converted, as above mentioned, into anethoïn, and by heating for several hours to 320°, partially into isanethol.

Isanethol is a light-yellow, viscid mass, resembling Venice turpentine; it does not alter at 380°, dissolves easily in ether, less easily in alcohol, and in contact with oil of vitriol is converted into anethoïn.

Anethol heated with 2 pts. of strong *hydriodic acid* in a flask with upright condensing tube, gives off methyl-iodide amounting to about 50 p. c. of the anethol used. Hence it is probable that anethol is the methylic ether of an allyl-phenol, and that its rational formula is $C^6H^4\begin{cases} OCH^3 \\ C^3H^5 \end{cases}$ (Ladenburg a. Leverkus, *Ann. Ch. Pharm.* cxli. 260). This phenol, $C^9H^{10}O$, has lately been obtained by Ladenburg by prolonged heating of purified anise-oil with potassium hydrate. (See Anol.)

When oil of anise, or the compound $C^{10}H^{12}O.HCl$, formed by direct addition of hydrochloric acid to anethol (i. 298), is treated with sodium amalgam, and the product is subjected to fractional distillation, a liquid is obtained which boils between 220° and 224°, and is intermediate in composition between anethol and the compound $C^{10}H^{14}O$, containing 2 at. hydrogen more (Ladenburg, *Deut. Chem. Gesellsch.* 1869, p. 371; *Zeitschr. f. Chem.* [2] v. 576).

Anethol Bromide, $C^{10}H^{12}Br^2O$, is produced by adding bromine to anethol dissolved in ether, and remains, on evaporating the ether, as a crystalline very deliquescent mass, which gives off hydrobromic acid. By recrystallisation it is obtained in needles melting at about 15° (Ladenburg, *loc. cit.*).

Compound of Anethol with Quinine. $C^{10}H^{12}O.2C^{20}H^{24}N^2O^2.2H^2O$.—Crystallises from a hot alcoholic solution of 5 pts. quinine and 1 pt. anise-oil, and may be rendered colourless by recrystallisation, with addition of animal charcoal. The dry compound, which scarcely smells of anise-oil, gives off the whole of its water and alcohol at 100°–110° without fusion; it is decomposed by hydrochloric acid, but not by cold water; crystallises from ether in monoclinic prisms and tables, from alcohol mostly in acute four-sided double pyramids, having all their summits truncated (O. Hesse, *Ann. Ch. Pharm.* cxxiii. 382).

Chloranethol, $C^{10}H^{11}ClO$, is produced by leaving anethol in contact for some hours with phosphorus pentachloride, and treating the resulting granular mass with water (Kraut a. Schlun, *loc. cit.*); also by the action of the pentachloride on oil of anise (Ladenburg). It is a somewhat yellowish liquid, which solidifies at low temperatures, melts at −6°, and boils at 257°, giving off a small quantity of hydrochloric acid. Sp. gr. 1·154 at 0°. Heated with potash it gives off HCl, and is converted into a liquid, $C^{10}H^{10}O$, which, however, is difficult to obtain quite free from chlorine. This liquid has an unpleasant odour, is insoluble in water, boils at 240°–242°, and gives no precipitate with an ammoniacal solution of silver or copper. Chloranethol is not attacked by potassium acetate even at high temperatures, but when heated to 250° with silver acetate, it yields a distillate partly consisting of anisic acid (Ladenburg, *Zeitschr. f. Chem.* [2] v. 575).

ANGELIC ACID. $C^5H^8O^2 = \begin{matrix} CH(C^3H^6)'' \\ | \\ COOH \end{matrix}$ (p. 41).—This acid occurs as a glyceride in croton oil, and may be obtained from that oil, together with crotonic acid, by saponification (ii. 112). It is produced, together with an alcoholic substance called laserol, by heating laserpitin (v. 1091) with strong potash-ley, especially in presence of alcohol:

$$\underset{\text{Laserpitin.}}{C^{24}H^{36}O^7} + H^2O = \underset{\text{Laserol.}}{C^{14}H^{22}O^4} + \underset{\text{Angelic acid.}}{2C^5H^8O^2}$$

The angelic acid may be distilled off from the acidulated product with water (Feldmann, *Ann. Ch. Pharm.* cxxxv. 236).

Angelic acid heated to 180°–200° for eight hours with hydriodic acid and red phosphorus is completely converted into valeric acid (Ascher, *Zeitschr. f. Chem.* [2] vi. 217).

Bromangelic Acid. $C^5H^8Br^2O^2$ (Jaffé, *Ann. Ch. Pharm.* cxxxv. 291).—This acid is formed on gradually mixing 1 pt. of angelic acid, well cooled under water, with 2 pts. of bromine, as a viscid mass which crystallises after a while, and may be purified by conversion into a potassium salt and separation with hydrochloric acid. It then forms a white crystalline mass, which melts with partial decomposition at 76°, and dissolves sparingly in water, easily in alcohol and ether. It is inodorous, has an acid taste and reaction, decomposes carbonates, and forms with the alkalis and alkaline earths easily soluble salts, with the heavy metallic oxides easily decomposible precipitates. The *potassium-salt*, $C^5H^7KBr^2O^2$, forms sweet-tasting crystalline laminæ, and decomposes in aqueous solution even at ordinary temperatures, more quickly at the boiling heat. The *lead* and *silver salts* form white precipitates which decompose readily, with formation of metallic bromide. The *ethylic ether*, $C^5H^7(C^2H^5)Br^2O^2$, obtained by distilling an alcoholic solution of the potassium-salt with sulphuric acid, is a yellowish liquid having an odour of peppermint, and decomposing partially at about 185°.

Bromangelic acid is an addition-product, not a substitution-product, and is isomeric with dibromovaleric acid; in fact, angelic acid behaves to bromine just in the same manner as fumaric, maleic, and the pyrocitric acids (p. 48). On the other hand, angelic acid shows little or no tendency to pass into a saturated acid by taking up nascent hydrogen. Its lower isomeride, acrylic acid, $C^3H^4O^2$, is converted by sodium amalgam into propionic acid, $C^3H^6O^2$; but angelic acid when thus treated does not yield valeric acid; and bromangelic acid treated with sodium amalgam is merely resolved into sodium bromine and angelic acid; when heated with hydriodic acid in sealed tubes, it yields merely traces of valeric acid, recognisable by its odour. Potassium bromangelate heated with water gives off carbon dioxide, and yields a brominated oil, C^4H^7Br, which boils with partial decomposition at 97°:

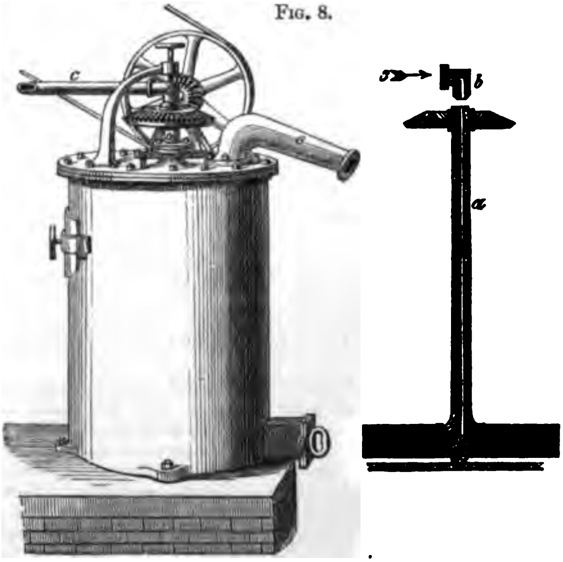
$$C^5H^7KBr^2O^2 = CO^2 + KBr + C^4H^7Br.$$

This oil has a pungent tear-exciting odour, and (like bromangelic acid itself) yields, when treated with excess of potash, a gas, probably quartine or crotonylene, C^4H^6, which smells like allylene, burns with a bright flame, is absorbed by water and by bromine, and is not precipitated by ammoniacal silver solution. The oil C^4H^7Br is decomposed by silver acetate, yielding silver bromide, and probably also crotyl acetate; it unites with bromine, producing rise of temperature, and forming a viscid non-distillable oil, $C^4H^7Br^3$. Hence the brominated compound C^4H^7Br behaves on the one hand like bromobutylene, and on the other like crotyl bromide, the homologue of allyl bromide (Jaffé).

ANILINE. This name is applied sometimes to pure phenylamine, C^6H^7N or $C^6H^5.H^2.N$, sometimes to the mixture of phenylamine and toluidine, which is obtained by reduction of commercial nitrobenzol, and used for the manufacture of aniline-red. We shall here use it in the latter sense, designating the pure base C^6H^7N, as phenylamine or amidobenzene.

Manufacture of Aniline.—The preparation of aniline by the reducing action of ferrous acetate on nitrobenzol is shortly described at p. 421, vol. iv. The chief alterations that have been made in it consist in the reduction of the proportion of acetic acid, and the application of high pressure or superheated steam for the distillation. The apparatus used consists of a cast-iron cylinder (fig. 8), having a capacity of about 1,000 litres. In the axis of this cylinder there is a hollow shaft or spindle *a* carrying a stirrer *d*, and worked by bevelled wheels, to which motion is given by a steam engine. The shaft *a* is ground to an elbow *b*, connected with the steam-main *c*, and held down by a screw, so that when the steam is turned on, it passes through the hollow elbow down the shaft, and then blows out at the bottom *d* among the products. In this manner the aniline is volatilised and passes with the steam through the neck *e* into a worm not shown in the figure, by which it is condensed.

FIG. 8.



To start the operation, 10 kilograms of acetic acid of 8° Bm. (sp. gr. 1·060), diluted with six times its weight of water—or rather with the acid liquid obtained in a previous distillation of aniline—are poured into the vessel through an aperture at the top; 30 kilogs. of pulverised cast iron and 125 kilogs. of nitrobenzol are added; and the stirrer is set in motion. The temperature quickly rises, and a brisk reaction takes panied by disengagement of vapour and the commencement of distillation.

From this time fresh quantities of the finely divided iron are added till the total quantity amounts to 180 kilogs. The stirrer is kept in motion during the whole operation, and should not be stopped till an hour or two after the last additions of iron. The heat produced by the reaction gives rise to a copious distillation of acid water and nitrobenzol, together with traces of benzol. These products collect in a receiver placed below the worm, and are returned to the cylinder from time to time. In some manufactories, the nitrobenzol, instead of being introduced all at once, is made to flow into the cylinder in a continuous fine stream; in this case the whole of the iron is introduced at the commencement of the operation.

At the end of the reaction, the cylinder contains a brown-red mass composed essentially of ferric hydrate, aniline, acetic acid, and unaltered iron. To extract the aniline, the stirrer having been kept in motion for an hour or two longer, and the mass then left at rest for some hours, steam is blown through the shaft, in small quantities at first, till the whole mass is raised to the boiling point. The aniline and other volatile products are then carried forward by the steam, and, passing out by the neck *e*, are condensed by the worm and collected in a receiver below.

Some manufacturers, however, prefer distillation over the open fire. In this case, the cylinder having been left to cool after the termination of the reaction, the brown semifluid mass is removed by the large aperture *b* at the bottom, and distilled without previous neutralisation, either in iron cylinders like gas-retorts, or in small cast-iron alembics. This mode of distillation is said by some authorities to be more economical than that in which steam is used; also to give for the most part a more abundant product, better adapted for the manufacture of rosaniline. Aniline distilled in this manner generally contains acetanilide.

By the processes above described, 125 kilogs. of nitrobenzol may be converted into aniline in 12 hours in each cylinder of 1,000 litres.

The crude product of the distillation contains water, acetic acid, acetone, benzol, and aniline. To get rid of the adventitious substances, it is strongly supersaturated with alkali, whereby the water is completely separated, and the oily mixture is decanted and rectified. Acetone then passes over first, then benzol (always a sign of bad preparation), and lastly, from 180° to 230°, the aniline. A second rectification, generally between 180° and 210°, yields it in the state in which it is found in commerce. Some manufacturers mix the aniline before rectification with quicklime, which retains all the acetic acid and the water.

The residues left after the second distillation are called 'queues d'aniline;' they have been examined by Hofmann, who has obtained from them the bases paraniline, tolylene-diamine, and xenylamine or martylamine (iv. 352; v. 872, 1054).

ANILINE COLOURS. The manufacture and applications of these colours have received considerable extensions since the account of them in vol. iv. pp. 465–473, was written. We proceed to notice the more important of these extensions.

Aniline Black. Lauth's method of obtaining this colour (iv. 466) has been modified by Camille Koechlin, the alteration consisting in replacing the hydrochloride of aniline by the tartrate, a salt which does not injure even the most delicate tissues, and has also the advantage of not attacking the mordants with which it is mixed for printing. The tartrate of aniline by itself would not be capable of producing aniline black; but in presence of sal-ammoniac, the proportion of which is considerably increased in this modified process, double decomposition, resulting in the formation of aniline hydrochloride, gradually takes place upon the tissue.

The improved process consists in boiling together 10 litres of water, 2 kilogs. of starch, 2 kilogs. of roasted starch, 2 kilogs. of aniline, 1 kilog. of sal-ammoniac, and 1 kilog. of potassium chlorate; then when the mixture has cooled, and immediately before printing, adding 1 kilog. of cupric sulphide and 2 kilogs. of tartaric acid. The cupric sulphide may be advantageously prepared by dissolving 1 kilog. of flowers of sulphur without the aid of heat in 4 litres of caustic soda of 38° Bm., and adding this liquid to a solution of 5 kilogs. of cupric sulphate in 120 litres of water, the solution being heated to 120°.

Various other processes have been recently published for the preparation of aniline black, but hitherto they have not practically replaced the process with cupric sulphide. Higgin of Manchester recommends the use of the arsenate, tungstate, or oxide of chromium, together with chlorate of potassium and hydrochloride of aniline (*Bull. Soc. Chim.* [2] vii. 93). There is also an aniline black called 'Lucas black,' the composition of which is kept secret; it is sold in the form of a paste containing all the elements necessary for the production of the black, and requiring only to be thickened and printed in order to develop the colour. Dullo (*Illustr. Gewerbezeit.* 1866, p. 161) prepares an aniline black in the form of paste, by mixing 100 grms. of light aniline (heavy aniline gives brown instead of black) with 80 grms. of hydrochloric acid, 10 grms. of manganese dioxide, and 1,000 grms. of water. The precipitate is washed by decantation, and then mixed with ammonia, whereupon its colour changes from green to black, and if the absorption of oxygen from the air be assisted by due agitation, the colour becomes developed throughout the entire mass.

The composition of aniline black is not known, neither is its mode of formation thoroughly understood; but it appears to depend upon oxidation of the aniline by the potassium chlorate and the cupric sulphide, which being successively reduced by the aniline and reoxidised by contact with the air, act as carriers between the oxygen of the air and the aniline. The sal-ammoniac, the presence of which is very useful, if not indispensable, appears to act by dissolving the cuprous compounds as they are formed, and thereby facilitating their reoxidation.

Aniline black is much valued for printing on calico, on account of its brilliancy and permanence. It acquires a greenish hue by long exposure to light and air, but may be brought back to its normal colour by treatment with alkaline solutions. It has not hitherto been successfully applied in practice to the dyeing of silk and wool, but the difficulties which this application of it presents will perhaps be overcome. Lightfoot, the discoverer of aniline black, has shown that it may be fixed on wool if the wool has been previously oxidised with chloride of lime (*Chem. News*, 1866, p. 59); and, still more recently, Jules Persoz has succeeded in dyeing wool with aniline black by mordanting it with a mixture of potassium bichromate and cupric sulphate, and then passing it through a solution of aniline. The difficulty of fixing the black on animal fibres appears to be due to the fact that it is precipitated in flocks too large to penetrate into their pores (*Dictionnaire de Chimie*, i. 326).

Aniline Blue. Of all the blue compounds produced by the reaction of the different reagents upon aniline, the only one that has come into practical use as a dye is the 'bleu de Lyon,' or triphenyl-rosaniline, obtained by heating a salt of rosaniline with aniline (iv. 472). To obtain it of fine quality, it is found necessary to use a salt of rosaniline containing an organic acid. The mixture which is found to answer best consists of 10 kilogs. of crystallised rosaniline acetate, 30 kilogs. of aniline (containing but little toluidine, and therefore boiling at a low temperature), 1·5 kilog. of benzoic acid, and 2·2 litres of caustic soda solution of 38° Bm. (sp. gr. 1·333). This mixture is heated in an enamelled cast-iron pot, which is placed over an oil-bath set in brickwork and closed with a lid, through which passes an escape-tube connected with a condensing worm. The bath is heated for about three hours, the temperature being gradually raised from 180° to 210°. At first the red colour of the mixture changes slowly, but afterwards rapidly; the change is complete when a drop of the mixture spread out on a glass plate with a little hydrochloric acid appears of a pure blue colour without mixture of violet by candle or gas light.

The following process, communicated by M. Bardy to Wurtz's *Dictionnaire de Chimie*, affords the means of preparing at the same time a fine blue and a fine violet dye (*violet impérial*).

Rosaniline hydrochloride is mixed with 30 p. c. of its weight of sodium acetate; the mixture is evaporated to dryness; free aniline is then added, together with a quantity of crystallised potassium acetate equal to 10 p. c. of the rosaniline salt; and the mixture is heated to 175° till the whole assumes a pure blue colour. The product is then removed from the boiler and dissolved, with aid of heat, in one and a half times its weight of strong hydrochloric acid. The blue compound, insoluble under these circumstances, floats on the surface; it is collected, washed with water, and treated with five times its weight of caustic soda at 32°; and the mixture, after boiling for twenty minutes, is diluted with 15 parts of boiling water and filtered. The base thus obtained is purified from traces of mono- and diphenyl-rosaniline by washing with tepid alcohol, then dissolved in its own weight of sulphuric acid diluted with 10 pts. of water; the liquid is boiled for ten minutes and filtered; and the blue deposit left on the filter is washed.

The hydrochloric acid solution is diluted with a quantity of water equal to 1⅛ pt. of the weight of the crude blue, whereby a precipitate is formed consisting of diphenyl-rosaniline; then again with 23 pts. of water, which throws down monophenyl-rosaniline. The mother-liquors of this second precipitate, saturated with lime and mixed with acetate and chloride of sodium, yield a considerable quantity of very pure hydrochloride of rosaniline.

Aniline blue is insoluble in water, and this circumstance forms a great drawback to its use, inasmuch as when employed for dyeing, it is thrown out of solution in the dye-bath, and then mechanically adheres to the goods, so that it afterwards rubs off. It may indeed be kept in solution by the use of large quantities of alcohol, but this treatment greatly adds to its cost.

Mr. Nicholson has, however, discovered an economical method of rendering this blue perfectly soluble in water, namely by the use of strong sulphuric acid, with which it appears to form a sulphocongugated acid, analogous to sulphindigotic acid. The blue is first boiled with dilute sulphuric acid, to remove all substances soluble therein, and the residue, after thorough drying, is treated with strong sulphuric acid of 66° Bm. (sp. gr. 1·842), which dissolves it. The solution is heated to 150° for half an hour, then diluted with 4 volumes of water and filtered. That which remains on the filter is the blue in its soluble modification, but rendered insoluble for the time by the presence of the sulphuric acid. It is washed several times with water, cautiously when the acidity of the water becomes considerably reduced, as the modified blue, though insoluble in the dilute acid, is easily soluble in pure water.

An improvement on the mode of preparing the soluble blue has been made by Max Vogel (*Bull. Soc. Chim.* 1866, ii. 253), who heats 1 pt. of the insoluble blue to 130° for six hours with 8 pts. of fuming sulphuric acid. Leonhardt obtains a peculiar modification of aniline blue by dissolving it in alcohol and precipitating with water. The product thus formed easily diffuses through water, and remains suspended in a state of very minute division which greatly facilitates the dyeing. It is in fact identical in every respect with that which is produced by the dyer himself in the boiler, but its preparation in a chemical manufactory affords the means of recovering the alcohol, which would otherwise be completely lost. A similar result is obtained by dissolving ordinary aniline blue, without the aid of heat, in strong sulphuric acid and precipitating with water. Under these circumstances no sulpho-acid is formed, but merely a solution analogous to that of alizarin in sulphuric acid (Monnet a. Drury, *Dictionnaire de Chimie*, i. 323).

Soluble aniline blue is much used for silk-dyeing, but it is thought not to be so fast as the normal compound. A modification of it, known commercially as 'Nicholson's blue,' is now very extensively used in Great Britain for wool-dyeing, but its application does not appear to be understood in France and Germany.

Another soluble aniline blue, called 'bleu de Paris,' was discovered by Persoz de Luynes and Salvétat. It is prepared by heating aniline with stannic chloride to 180° for thirty hours. It is generally described as probably identical with the 'bleu de Lyon,' but is in reality quite different, being easily soluble in water, and crystallising freely in blue needles with a copper reflex. It consists of the hydrocloride of an organic base, which is precipitated from its solution by alkalis as a purplish-blue powder. It dyes silk readily and retains its blue colour by artificial light; but it is difficult to prepare in large quantities, and has never been introduced commercially.

Toluidine blue has been already described (iv. 472).

Diphenylamine blue.—The formation of compounds having a fine blue colour, by the action of various reagents on diphenylamine, was first pointed out by Hofmann (iv. 453); but the discovery of a diphenylamine blue adapted for use in dyeing is due to Girard a. De Laire (*Bull. Soc. Chim.* [2] vii. 360). They prepare it by heating to about 230°, under pressure or in an open vessel with continual recondensation of the vapours, a mixture of 1 mol. of pure aniline and 1½ mol. of aniline hydrochloride.

The transformation of diphenylamine into a blue dye may be effected by heating 2 pts. of the base with 3 pts. of carbon trichloride to about 160° for several hours. Hydrochloric acid and carbon dichloride are then evolved, and the mass is converted into a bronze-coloured product, which must be washed with benzol and petroleum, and then dissolved in alcohol or wood-spirit; the filtered solutions, precipitated with twice their volume of hydrochloric acid, yield the blue almost pure and amounting to 40 p. c. of the diphenylamine employed. Another process consists in heating diphenylamine to 110°–120° for three to five hours with an equal weight of oxalic acid; but the product thus obtained is not very abundant (Brimmeyr, *Dingl. pol. J.* clxxxv. 49).

Diphenylamine blue yields very pure colours in dyeing. Its composition is probably the same as that of triphenyl-rosaniline:

$$\underset{\text{Diphenylamine.}}{2C^{12}H^{11}N} + \underset{\text{Ditolylamine.}}{C^{14}H^{15}N} - H^{6} = \underset{\text{Triphenyl-rosaniline.}}{C^{38}H^{31}N^{3}}$$

It can be produced only with a mixture of diphenylamine and ditolylamine. Pure diphenylamine similarly treated yields a blackish blue, ditolylamine a maroon-brown, and phenyl-toluidine a bluish-violet.

Aniline Greens. 1. One of the most important of these colouring matters, specially designated as 'aldehyde green,' was discovered in a remarkable manner. Towards the end of 1861 Lauth obtained a blue colour by the action of aldehyde on a solution of a rosaniline salt in sulphuric acid. This product had a magnificent blue colour, but was found to be utterly unstable, and therefore useless as a dye. It was however experimented upon by Cherpin, a chemist in the dye-works of M. Usèbe, near St. Ouen; and he, finding himself unable to fix it, mentioned his difficulties to a photographic friend, who recommended him to try hyposulphite of sodium, as that salt was always used for 'fixing' photographs! Cherpin followed this counsel, but instead of fixing his blue, he found that it was changed into a splendid green dye, now known as 'aldehyde green.'

To prepare this colouring matter, about 1½ pt. of aldehyde is gradually added to a cold solution of magenta, prepared by dissolving 1 pt. of the latter in 3 pts. of strong sulphuric acid and 1 pt. of water. The mixture is then heated in a water-bath till a drop of the product diffused in water produces a fine blue coloration, and then poured into a large quantity of boiling water containing three or four times as much sodium hyposulphite as the magenta employed. After boiling for a short time, the liquid is filtered off from a greyish insoluble residue which forms. The filtrate contains the green. This process being a very simple one, many dyers now prepare the green colouring matter as they require it. It may, however, be precipitated by means of tannin or sodium acetate, collected on filters, and drained to a paste, or, if necessary, dried. It is found in the market in both these forms. Hirzel (*Deutsche Industrie Zeitung*, 1864, No. 31, p. 307) prepares this colour by treating a solution of the aldehyde blue with ammonium sulphydrate instead of the hyposulphite, heating the mixture till it turns green, then filtering and treating the green solution as above.

The composition of aldehyde green is not exactly known; but, according to Lauth, it contains sulphur as an essential constituent, and is produced whenever a solution of aldehyde blue is brought in contact with nascent sulphur. This view is in accordance with results recently obtained by Hofmann. According to E. Lucius, on the contrary, the aldehyde green exists ready formed in an acid solution of a rosaniline salt mixed with aldehyde; and the sodium hyposulphite acts merely by removing the blue or violet substances which are always formed at the same time; the same separating action is indeed exerted, not only by hydrogen sulphide and sulphurous acid, but by animal charcoal, silica, flowers of sulphur, &c. (*Patents*, 1864, Nos. 200 and 301).

Aldehyde green is undoubtedly the salt of an organic base, and this base may be separated from it by decomposing an aqueous or alcoholic solution with soda or ammonia, most readily by operating on the product precipitated with sodium acetate. The base is of a pale green colour, like chromic hydrate; it is slightly soluble in alcohol, and the solution is completely altered by boiling. It dissolves in acids, forming bright green but very unstable salts, and is changed to the normal colour of aldehyde green by absorbing carbonic acid from the air.

Aniline green is principally employed in silk dyeing. It is a splendid colour, and very brilliant both by day and by artificial light.

2. *Green produced by the ethylation or methylation of Rosaniline or of Methylaniline violet.*—This green, known commercially as 'iodine green,' appears to have been discovered by several chemists at nearly the same time. Its preparation, which has been described successively by Tillemans of Crefeld, by Lucius (*Jahresb.* 1864, p. 818), by Poirrier a. Chappat (*Bull. Soc. Chim.* [2] vi. 504), and by Wanklyn a. Paraf (*ibid.* vii. 269), consists in subjecting the violets of triethyl- or trimethyl-rosaniline (Hofmann's violet), or the violets of methylaniline to the action of an excess of alcoholic iodide. The process given by the last-mentioned chemists is as follows: A mixture of equal parts of rosaniline, methyl alcohol, and an alcoholic iodide is heated for three hours to 110°; and the product of the reaction is washed with sodium carbonate, which dissolves a small quantity of green colouring matter, leaving the greater part of the product in the form of an insoluble salt, which is in fact Hofmann's violet. This latter is decomposed by a caustic alkali, so as to set the base at liberty; and this base, after being dried and pulverised, is again subjected to the action of the alcoholic iodide; a third operation carried out in the same manner converts nearly all the violet into green. The product, being soluble in water rendered slightly alkaline with sodium carbonate, may thus be easily separated from the foreign matters which accompany it, as well as from the violet salt which remains unaltered.

The green thus obtained with methyl iodide has a very fine colour, and, like the aldehyde green, preserves its character by artificial light. It is much used for cotton and silk dyeing; its colour is bluer than that of aldehyde green, and it is therefore more useful, as it yields with picric acid a greater variety of green shades.

Important observations on the manufacture and constitution of 'iodine green' have lately been published by Hofmann a. Girard (*Deut. Chem. Gesellsch.* Berlin, 1869, p. 440; *Zeitschr. f. Chem.* [2] v. 652). The following proportions yield a satisfactory result: 1 pt. rosaniline acetate, 2 pts. methyl iodide, and 2 pts. methyl alcohol. The methyl iodide might be replaced by bromide (1·3 pt.), but in the manufacturing process the iodide is preferred.* The reaction takes place in large closed boilers (autoclaves) of enamelled wrought or cast iron, capable of sustaining a pressure of 25 atmospheres, and surrounded by jackets in which a stream of boiling water circulates for eight or ten hours. The operation is then completed and the boiler is left to cool. It then contains a mixture of violet and green colouring matter dissolved in methyl alcohol, together with considerable quantities of methyl acetate and methyl oxide, which latter escapes with violence on opening the boiler. The volatile products having been removed by distillation, the residual pasty mass of colouring matters is poured into a large quantity of boiling water, whereby the green is completely dissolved, while the violet remains undissolved, with the exception of a small quantity held in solution by the acid set free during the reaction. The insoluble violet is separated by filtration, and the small quantity dissolved is precipitated by addition of common salt, after the free acid has been neutralised by sodium carbonate. To hit the exact point of saturation in the deep-coloured liquid, a sample is filtered from time to time, and, instead of litmus-paper, a thin skein of silk is introduced into the filtered liquid: as soon as the silk acquires a pure green colour without any admixture of violet, the addition of sodium carbonate may be discontinued, the precipitation of the violet colour being then complete. The liquid when quite cold is finally passed through a sand filter to remove the precipitated violet; and the green is precipitated by a cold-saturated solution of picric acid. The picrate of iodine green thus obtained, being but slightly soluble in water, is rapidly washed therewith, and, after evaporation, sold to the dyers in the form of paste. The violet colouring matters obtained in the preceding process in the form of iodides are converted into the corresponding bases by means of sodium hydrate, and from these bases further quantities of iodine green may be obtained by treatment with methyl iodide.

To obtain *crystallised iodine green*, the coloured product of the reaction is poured into a quantity of water, much smaller than that used in the process above described, and after addition of common salt, the liquid is mixed with a larger quantity of sodium carbonate, in order to ensure the complete precipitation of the violet. The filtrate on cooling deposits a considerable quantity of iodine green in crystals, which may be washed once or twice with cold water to remove adhering common salt, and then dried at the temperature of the air. To obtain the compound quite pure and in a state fit for analysis, the crystals are dissolved in warm absolute alcohol, and the filtered solution is poured into a large excess of absolutely anhydrous ether, whereby a shining crystalline precipitate is formed, which is washed on a filter with cold ether, and, after evaporation of the ether, dried over sulphuric acid. Lastly, the crystalline precipitate is dissolved in warm alcohol, which on cooling deposits chemically pure iodine green in splendid prisms, having the peculiar metallic lustre of the wing-cases of cantharides. When dried over sulphuric acid they consist of

Methyl-iodide of trimethyl-rosaniline, $C^{20}H^{16}(CH^3)^3N^3\left\{\begin{matrix}CH^3I\\CH^3I\end{matrix}\right. + H^2O$.

If left in a vacuum for forty-eight hours they give off 1 mol. water, and if left still longer, the compound undergoes further decomposition.

The corresponding *chloride*, obtained by decomposing the iodide with silver chloride, dries up to a green transparent brittle vitreous mass. The solution yields with platinic chloride a brown amorphous precipitate consisting of the *platinochloride*:

$$C^{20}H^{16}(CH^3)^3N^3\left\{\begin{matrix}CH^3Cl\\CH^3Cl\end{matrix}\right.PtCl^4.$$

The *picrate*, $C^{20}H^{16}(CH^3)^3N^3\left\{\begin{matrix}(CH^3)C^6H^2(NO^2)^2O\\(CH^3)C^6H^2(NO^2)^3O\end{matrix}\right.$, separates on adding picric acid to the aqueous solution of the iodide, as a dark green precipitate, which, by recrystallisation from boiling alcohol, yields the salt in well-defined prisms, yellowish by transmitted light, and shining like etched copper in reflected light.

The *acetate* crystallises in slender needles, the *nitrate* in prisms. These salts are

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* Considering the comparatively small equivalent of bromine, and the low price at which it may now be obtained from the Stassfurt salt-works, it is remarkable that so few attempts should hitherto have been made to substitute it for iodine in manufacturing processes. So far as the preparation of aniline colours is concerned, the chief difficulty in the use of the bromides of methyl and ethyl arises from their low boiling points (13° and 14°), in consequence of which large quantities of these compounds are lost. This difficulty may, however, be surmounted by using, instead of these bromides ready prepared, a mixture of methyl or ethyl alcohol with amyl bromide, a compound easily prepared, and boiling at 120°. In the first stage of the reaction which then takes place, amyl alcohol is formed, together with methyl or ethyl bromide, thus:

$$C^5H^{11}Br + CH^3OH = C^5H^{11}OH + CH^3Br;$$

and the bromide of methyl or ethyl thus obtained brings about the methylation or ethylation of the aniline base nearly as well as the pure compounds (Hofmann a. Girard).

obtained by treating the free base with acetic and nitric acid. A compound of the *iodide* with *zinc iodide*, obtained by precipitating the iodide with acetate or sulphate of zinc, crystallises from hot water in prisms not altered at 100°. A solution of *tannin* precipitates a compound which has not been analysed.

Transformations of Iodine green.—The green crystals of the iodide, as already observed, undergo a gradual change when left in a vacuum. If crystals which have been thus left for some months are drenched with water, they partly dissolve, forming a green solution, and if this be poured off, the remaining crystals dissolve in alcohol with a fine violet colour. This transformation into a violet compound takes place in a few hours at the temperature of boiling water, and instantly at 130°–150°; thus the green iodide dissolves with splendid violet colour in boiling aniline. The violet compound consists of *methyliodide of trimethyl-rosaniline*, and is formed from the hydrated dimethyliodide by loss of water and methyl iodide:

$$\underset{\text{Green.}}{C^{20}H^{16}(CH^3)^3N^3\left\{\begin{matrix}CH^3I\\CH^3I\end{matrix}\right..H^2O} = \underset{\text{Violet.}}{C^{20}H^{16}(CH^3)^3N^3.CH^3I} + H^2O + CH^3I.$$

The formation of the violet colouring matter from the green iodide likewise takes place when a solution of the latter in methyl alcohol enclosed in a sealed tube is heated for two or three hours in the water-bath. The liquid then assumes a deep violet-blue colour, and deposits long cantharides-green needles of the compound

$$C^{20}H^{16}(CH^3)^3N^3.(CH^3I)^2,$$

which are but sparingly soluble in alcohol even at the boiling heat. These are best recrystallised from methylic alcohol, in which they are somewhat more soluble. The same compound is occasionally formed in the action of methyl iodide on trimethylrosaniline. Together with these sparingly soluble crystals, whose solution is violet with a decided tinge of blue, there is also formed another blue-violet salt, but less decidedly inclining to blue. This salt is extremely soluble in alcohol, but may be crystallised by slow evaporation of the alcoholic solution. It is identical with the violet salt above mentioned as obtained by the simple action of heat on the green iodide, namely $C^{20}H^{16}(CH^3)^3N^3.CH^3I$.

A molecule of the green iodide heated in methyl-alcoholic solution under pressure undergoes the same transformation as when heated in an open vessel; but the separated molecule of methyl iodide, which would escape into the air if it were not confined, fixes itself upon a second molecule of the green compound, converting it into the sparingly soluble violet compound with 2 mol. methyl iodide.

The green and violet iodides treated with alkalis are converted into the corresponding bases (hydrates), which are colourless. The base corresponding to the iodine green may also be obtained by decomposing a solution of the picrate in ammoniacal alcohol with soda-ley.

If in the preparation of iodine green, either the proportions of the materials, or the temperature, or the time of heating, differ considerably from those above described (p. 162), a colourless product is likewise obtained, which may be separated from the coloured products formed at the same time by means of hot alcohol, in which it is nearly insoluble. On dissolving it in water, evaporating, and recrystallising several times from dilute alcohol, this compound is obtained in prismatic crystals, having the composition of *trimethyliodide of pentamethylated leucaniline*: $C^{20}H^{16}(CH^3)^5N^3.(CH^3I)^3 + H^2O$. (See LEUCANILINE.)

3. A third kind of green, known commercially as 'Perkin's green,' resembles the iodine green more closely than the aldehyde green, but differs from it in solubility and in being precipitated by sodium carbonate. It contains an organic base, which is nearly colourless, and is by no means a chemically powerful body. Like the iodine green, it is precipitated by picric acid, forming a picrate which crystallises from alcohol in small prisms having a golden reflex.

This colour is now much used, chiefly for calico-printing.

Aniline Maroons and Browns. These colours, like the aniline yellows, possess only a second-rate industrial importance. Girard a. De Laire obtain a maroon by melting 4 pts. of aniline hydrochloride, projecting into the fused mass 1 pt. of rosaniline hydrochloride, and heating the mixture to 240°; it then quickly changes from red to maroon. The colouring matter thus obtained is soluble in water, and is precipitated therefrom by alkalis and alkaline salts.

A. Schultz prepares a fine garnet colour by passing a current of nitrous vapours into a solution of soda or ammonia holding rosaniline in suspension. The dye thus obtained produces on wool, silk, and cotton, fine shades varying from puce to garnet.

Horace Koechlin utilises the brown substances noticed by Hofmann in the oxidation of rosaniline; he fixes these browns on tissues by printing on wool a mixture of fuchsine, oxalic acid, and potassium chlorate; and on cotton the same, with addition of cupric sulphide. This brown may also be fixed upon cotton by means of albumin. It may be prepared in a state fit for this application by acting on fuchsine with potassium chlorate and hydrochloric acid. The product thus obtained is insoluble in water, soluble in alcohol and in strong sulphuric acid, and is precipitated from these solutions by water (*Moniteur scientif.* 1866, p. 262).

Jacobson (*Dingl. pol. J.* clxxvii. 405) describes two processes for obtaining aniline brown, viz. (1) Heating 1 pt. of picric acid to 140° with 2 pts. of aniline as long as ammoniacal vapours are disengaged; dissolving the product in dilute hydrochloric acid, and precipitating with caustic soda. (2) Heating a strong solution of ammonium chromate to 100°, together with aniline formate.

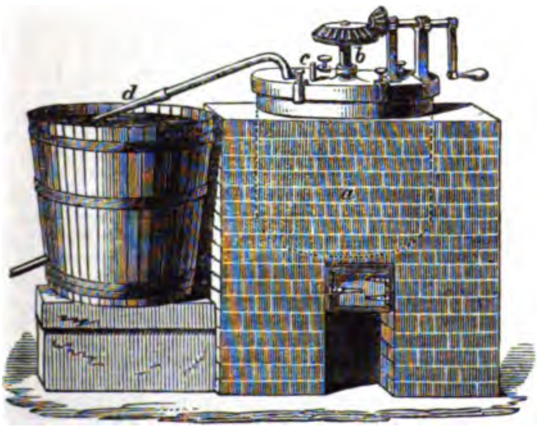
Wise heats to 140° a mixture of 1 pt. rosaniline, 1 pt. formic acid, and ½ pt. sodium acetate, and thereby obtains a substance which dissolves in alcohol with a fine scarlet colour. On heating this substance with three times its weight of aniline, it is transformed into a product having a rich brown colour (*Bull. Soc. Chim.* 1866 [2] vi. 431; *Dictionnaire de Chimie*, i. 329).

Aniline Pink, also known commercially as 'safranine,' is a colouring matter much redder than magenta, produced by oxidation of aniline. It was discovered some years ago by Perkin, and is now employed to a limited extent in the arts. It appears to be an organic base composed of $C^{18}H^{18}N^4$. It gives crimson solutions with acids, forms crystallisable salts, and its reactions show that it is closely related to mauveine (Perkin, *Proceedings of the Royal Institution*, 1869).

Aniline Red. *Fuchsine, Magenta, &c.*—The use of arsenic acid for the preparation of this colour has nearly superseded all others. In the description of this process given in vol. iv. p. 468, it is stated that 12 pts. of the dry acid of commerce are to be heated with 10 pts. of aniline, *with or without addition of water.* Experience has shown, however, that the addition of water is absolutely necessary to the success of the process.

The manufacture of magenta is now conducted in an apparatus similar to that represented in fig. 9. This apparatus consists of a large iron pot, *a*, about 4 ft. in diameter, set in a furnace of brickwork, and provided with a stirrer worked by hand. All the gearing for this stirrer is fixed to the lid, so that stirrer, lid, and all may be lifted away by means of a crane, or other suitable apparatus. There is also a bent tube fixed into the lid, and connected with a condensing worm, *d*, by means of a joint, which can be made or broken at pleasure. In preparing magenta, a quantity of aniline containing about 25 per cent. of toluidine, and a nearly saturated solution of arsenic acid, are introduced into this apparatus, and well mixed by working the stirrer; the proportion of the materials is in about the ratio of 1 of aniline to 1·5 of a 75 per cent. solution of arsenic acid. When these are well mixed, the fire is

FIG. 9.



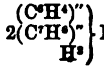
lighted. After the product has been heated for some time, water begins to distil over, then aniline and water, and, lastly, nearly pure aniline.

This operation requires some hours for completion, and this is determined by inserting an iron rod from time to time, and drawing out a portion of the product for examination, as well as by the amount of aniline which distils over. When the heating has been completed, a steam-pipe is introduced into the apparatus, and steam blown through the fused mass; by this means an additional quantity of aniline is separated. The lid is then liberated and lifted, with the stirrer, from the apparatus, and the product left to cool before it is removed. A more elaborate and larger apparatus is sometimes used, which possesses considerable advantages over the smaller one. The iron pot is larger, and is provided with an outlet at the side, which is closed during the operation, and the shaft of the stirrer is hollow (as in the aniline apparatus, fig. 8), and worked by steam. When the operation of heating is concluded, steam is blown down the shaft, and, after the addition of water, the product is boiled and run out of the outlet in the side of the pot; by this arrangement it is unnecessary to disconnect the lid of the apparatus, and the product does not require to be removed by mechanical means, as with the apparatus previously described.

The crude product obtained by heating aniline and arsenic acid is next transferred to vats, boiled with water and filtered. Common salt is then added, which precipitates the crude magenta: this is collected and dissolved in boiling water, again filtered, and the solution on cooling deposits the colouring matter in the crystalline state. This, when recrystallised, constitutes commercial magenta (Perkin's *Lectures on Coal-tar Colours*).

The several varieties of commercial aniline red have been shown by Hofmann to be salts of a colourless base, rosaniline, $C^{20}H^{19}N^3$, derived from 1 mol. of phenylamine and 2 mols. of toluidine, by elimination of 3 mols. of hydrogen:

$$C^{20}H^{19}N^3 = C^6H^7N + 2C^7H^9N - 3H^2.$$

For its rational constitution, Hofmann gives the formula  $2\left.\begin{matrix}(C^6H^4)''\\(C^7H^6)''\\H^3\end{matrix}\right\}N^3$. Crystallised rosaniline is $C^{26}H^{19}N^3.H^2O$.

Rosenstiehl has shown (*Bull. Soc. industr. de Mulhouse*, 1868, p. 931; *Bull. Soc. Chim.* [2] xi. 267) that commercial fuchsine or magenta always contains, in addition to rosaniline, another red colouring matter, isomeric therewith. The formation of this new colouring matter is due to the presence of pseudotoluidine or paratoluidine in commercial aniline, a fact previously demonstrated by Rosenstiehl (*Bull. Soc. Chim.* [2] x. 192). Rosaniline prepared from a mixture of pure aniline and pure normal toluidine, and pararosaniline prepared in like manner from aniline and paratoluidine, resemble each other in tinctorial quality and power, and indeed in all their physical and chemical properties, excepting that pararosaniline, when precipitated by an alkali from a hot solution, remains amorphous, whereas rosaniline under the same circumstances is soon converted into crystalline scales; and that rosaniline when subjected to the reducing action of hydriodic acid yields aniline and toluidine, whereas pararosaniline similarly treated yields aniline and paratoluidine.

Moreover, it appears from recent experiments by Coupier, that red colouring matters, very closely resembling the rosaniline salts, may be prepared without the simultaneous action of aniline and toluidine, in fact, from nearly pure toluidine or xylidine without the aid of aniline at all; e.g. by heating a mixture of 100 pts. of Coupier's toluidine (which is liquid), 160 pts. of solution of arsenic acid (of 75 p. c.), and 35 pts. hydrochloric acid to 150°-160° for three or four hours; or 67 pts. *crystallised* toluidine, 95 pts. nitrotoluene, 65 pts. hydrochloric acid, and 7 pts. of ferrous chloride to 190° for three hours. Xylidine also yields red colouring matter when subjected to similar treatment.

Toluidine red possesses properties analogous to those of aniline red, but is distinguished from the latter by the bluer tint which it communicates to vegetable or animal fibres; by its more regular transformation into derivatives of other colours, especially green; by its greater depth of colour; and by its much greater solubility in water. It is, moreover, obtained in greater abundance from a given quantity of material, the yield amounting to 40 p. c. of the material employed, whereas that of aniline red seldom exceeds 30 p. c. The addition of aniline to the toluidine actually diminishes the quantity obtained, the diminution being directly proportionate to the quantity of aniline added. Xylidine red yields in dyeing more violet tints than toluidine red (*Bull. Soc. indust. de Mulhouse, avril et mai* 1866; *Bull. Soc. Chim.* [2] vi. 500; *Moniteur scient.* 1866, p. 599; *Dictionnaire de Chimie*, i. 319).

Coupier has also devised a process for the manufacture of aniline red in which the use of arsenic acid is avoided. It consists in heating to about 200° a mixture of pure aniline, nitrotoluene, hydrochloric acid, and a small quantity of metallic iron. The product is pasty and quickly solidifies to a friable mass resembling crude fuchsine (*Bull. Soc. Chim.* [2] xi. 269).

Aniline Violets. Of these dyes there are several varieties.

1. Mauve or Aniline purple, the first discovered of the aniline dyes. It consists of the sulphate or other salt of mauveine, $C^{26}H^{24}N^4$, a base which in the free state has a violet colour, and forms violet solutions. The rational formula of this base has not been determined; but it differs from rosaniline in not requiring for its formation the presence of toluidine; in fact, Perkin finds that it may be prepared by the oxidation of pure aniline (phenylamine) obtained from indigo. The same result has been obtained by Schützenberger.

Aniline purple is almost always prepared by oxidising aniline with potassium bichromate and sulphuric acid, the process originally given by Perkin. A patent has, however, been taken out by Dale and Caro for obtaining it by treating a salt of aniline with cupric chloride. Another mode of producing it is to heat a solution of aniline in hydrochloric acid with chloride of lime. When aniline hydrochloride is treated with a very dilute solution of chloride of lime, not in excess, a blue compound is produced, called Runge's blue; this indeed is the well-known reaction which gave rise to the name *Kyanol*, formerly applied to aniline. This blue is very unstable, but Perkin has lately succeeded in obtaining it in the solid state by treating a solution of aniline with dilute chloride of lime and adding common salt. The colouring matter is thereby precipitated in an impure state; but by treating it with cold ether or benzol, a large quantity of brown impurities is separated, and the Runge's blue is left in the solid state. It dissolves in alcohol, forming a blue or nearly blue solution, which, however, changes spontaneously into mauve in a day or two, and quickly on boiling. Silk dyed with the blue likewise assumes a mauve colour when steamed.

In France, aniline purple is sometimes manufactured by the action of chloride of lime on a solution of aniline in hydrochloric acid, the crude product being purified in the same manner as that obtained with bichromate. The product thus obtained is said to be more abundant than that yielded by Perkin's process; but the colour is more reddish and is not so highly valued.

2. Methylaniline Violets.—These dyes, produced by the oxidation of methylaniline and dimethylaniline, were discovered by C. Lauth (*Rép. Chim. app.* 1861, p. 345), and the methods of preparing them have recently been improved by Poirrier and Chappat (*Bull. Soc. Chim.* [2] vi. 502).

The preparation of methylaniline on the large scale is effected: α. By heating a mixture of aniline hydrochloride (100 pts.) and methyl alcohol (50 to 80 pts.) to 250° or 300° in enamelled iron vessels, for three or four hours. The product, consisting for the most part of methylaniline hydrochloride, is decomposed by an alkali and purified by distillation.—β. By heating to 300° for several hours a mixture of 100 pts. aniline, 50 to 80 pts. methyl alcohol, and 100 pts. sal-ammoniac; the product is methylaniline itself.—γ. By treating aniline with methyl nitrate, either in the cold or at 100°; in the latter case the reaction is very quick.—δ. By heating aniline with methyl chloride, either in an open vessel or under pressure. The product of either of these reactions is usually a mixture of methylaniline and dimethylaniline, the latter, of course, increasing with the quantity of methyl alcohol employed.

The methylated derivatives of aniline may be transformed into violet or blue-violet compounds, by the action of various reagents, e.g. by stannic chloride, mercuric iodide, iodine chloride, &c. The reaction usually takes place at about 100°, producing colouring matters which incline to blue in proportion as the aniline is more methylated; and in any case a violet once obtained may be rendered bluer by treating it after purification with an alcoholic iodide. The following are some of the processes recommended:—

α. Adding 5 to 6 pts. of stannic chloride by small successive portions to 1 pt. of methylaniline; heating the mixture to 100° till it becomes very thick; treating the product several times with a caustic alkali to remove tin; and purifying the resulting violet by the methods adopted for most aniline colours.—β. The stannic chloride may be replaced by iodine chloride diluted with 5 or 6 times its weight of water, or by a mixture capable of producing it: 100 pts. of methylaniline, for example, being treated with 20 pts. of iodine and 20 pts. of potassium chlorate.—γ. 1 pt. of methylaniline, 1½ pt. mercuric chloride, and 1 pt. potassium chlorate.—δ. 1 pt. of methylaniline, 3 pts. of mercuric iodide, and 1 pt. of potassium chlorate.—ε. 1 pt.

of methylaniline, and 3 to 4 pts. of benzene hexchloride, the mixture in this last case being heated to 150°–160°.

The violets obtained by these several reactions are soluble in water, alcohol, and acetic acid. They are fixed upon tissues by methods similar to those adopted for other aniline colours. Nothing is known respecting their composition.

3. **Mauvaniline and Violaniline.** These compounds are formed, together with a yellow body, chrysotoluidine, in the preparation of rosaniline by the oxidation of aniline with arsenic acid. It is well known indeed that the quantity of rosaniline obtained by this process does not amount to more than half of that which is indicated by theory, the second half of the aniline being converted into a black matter insoluble in water. These residues were for some time regarded as useless for the purposes of the dyer; but the recent experiments of Paraf (*Bull. Soc. Chim.* [2] vii. 92) have shown that they may be made to yield colouring matters available in dyeing and calico-printing; and these researches have been completed by Girard and De Laire (*ibid.* p. 366), who have obtained from these residues the bases above mentioned.

100 pts. of commercial aniline boiling at 183° to 188° (containing 2 pts. aniline to 1 pt. toluidine) are heated to 170° for five hours with 164 pts. of a solution of arsenic acid of the strength of 70 p. c. The product is exhausted with water, which dissolves arsenate of rosaniline, and the residue contains the arsenates of mauvaniline, violaniline, and chrysotoluidine, together with various impurities. The mixture of these salts is decomposed by boiling with caustic soda; and the precipitated bases are treated with dilute hydrochloric acid, which dissolves the mauvaniline and chrysotoluidine, leaving the violaniline undissolved. The hydrochloric acid solution is mixed with common salt, which precipitates hydrochloride of mauvaniline, while the chrysotoluidine salt remains in solution. The mauvaniline is precipitated from the solution of the hydrochloride by the addition of an alkali.

Violaniline, mauvaniline, rosaniline, and chrysotoluidine form a homologous series, as shown by the following formulæ:

$$\underset{\text{Violaniline.}}{C^{18}H^{15}N^3} = \underset{\text{Aniline.}}{2C^6H^7N} + \underset{\text{Aniline.}}{C^6H^7N} - 3H^2$$

$$\underset{\text{Mauvaniline.}}{C^{19}H^{17}N^3} = \underset{\text{Aniline.}}{2C^6H^7N} + \underset{\text{Toluidine.}}{C^7H^9N} - 3H^2$$

$$\underset{\text{Rosaniline.}}{C^{20}H^{19}N^3} = \underset{\text{Aniline.}}{C^6H^7N} + \underset{\text{Toluidine.}}{2C^7H^9N} - 3H^2$$

$$\underset{\text{Chrysotoluidine.}}{C^{21}H^{21}N^3} = \underset{\text{Toluidine.}}{C^7H^9N} + \underset{\text{Toluidine.}}{2C^7H^9N} - 3H^2$$

Mauvaniline is insoluble in water, soluble in alcohol, ether, and benzol, and forms crystals containing $C^{19}H^{17}N^3.H^2O$. Its salts are soluble in water, forming solutions of a fine reddish-violet tint, which they likewise impart to fabrics in dyeing.

Violaniline exhibits similar properties, but is insoluble in ether and in benzol. Its salts are not of much value for dyeing, as they produce merely dull bluish violet colours.

Mauvaniline treated with aniline yields phenylated derivatives analogous to the phenyl-rosanilines; with the iodides of ethyl and methyl it also forms ethylated and methylated derivatives similar to those obtained in like manner from rosaniline.

4. *Violets derived from Rosaniline.—a. Violet impérial.* The colouring matters known by this name are produced by heating a rosaniline salt with a quantity of aniline less than sufficient to form aniline blue. They were at first regarded as mixtures of aniline blue (triphenyl-rosaniline) with magenta, but Hofmann has shown that they are definite compounds, viz. monophenyl-rosaniline, $C^{20}H^{18}(C^6H^5)N^3$, and diphenyl-rosaniline, $C^{20}H^{17}(C^6H^5)^2N^3$, the former producing reddish-violet, the latter bluish-violet dyes. A method of obtaining these violet compounds simultaneously with aniline blue has already been described (p. 160).

β. Hofmann's Violets.—These compounds, consisting of triethyl- and trimethyl-rosaniline, are described in vol. iv. p. 471. They may be rendered soluble in water by liberating the base by means of a boiling solution of soda, and redissolving it in an acid (Duprey, *Bull. Soc. Chim.* [2] vii. 95).

Picrate of triethyl-rosaniline yields in dyeing very beautiful green tints (Keisser, *Moniteur scientif.* 1867, p. 536).

γ. Violets obtained by substitution of other radicles for the hydrogen of rosaniline.—By heating 6 pts. of magenta dissolved in 30 pts. of alcohol of 90 p. c. with 4 pts. of brominated oil of turpentine to 150° in a closed vessel for eight hours, Perkin has obtained a fine violet dye known as the *Britannia violet*. It possesses the golden-green lustre so common to all the aniline colours; is easily fusible, amorphous, and very soluble in water. It is very extensively employed for dyeing and printing, and can be produced of any shade from purple to a blue violet.

Wanklyn, by heating equal parts of rosaniline, alcohol, and isopropyl iodide to 100° in a closed vessel, obtains a violet compound, the base of which may be isolated by boiling with an alkali.

Smith and Sieberg (*Deutsche Industrie-Zeitung*, 1865, p. 488) employ for the same purpose the iodated and brominated derivatives of acetone.

Lastly, there is a dye called *Dahlia impérial*, of a very pure violet colour and soluble in water; but its preparation is kept secret.

Aniline Yellows. These colours have not yet attained any considerable importance in dyeing or printing. Chrysaniline, $C^{20}H^{17}N^3$, is described in vol. iv. p. 473.

Chrysotoluidine. $C^{21}H^{21}N^3.H^2O$.—The formation and preparation of this substance have been described in connection with mauvaniline (p. 168). It may also be obtained by heating crystallised toluidine, or the crude anilines distilling between 195° and 205°, with carbon trichloride. It is separated in the manner already indicated; the process may however be simplified by repeated treatment with zinc and hydrochloric acid, whereby the rosaniline is separated in the form of leucaniline.

Chrysotoluidine treated with alcoholic iodides yields fine roseate shades; with aniline it forms maroon-coloured products.

Diazo-amidobenzene and Amido-diphenylimide. $C^{12}H^{11}N^3$.—These isomeric compounds are both produced by the action of nitrous acid on an alcoholic solution of aniline, the former at ordinary, the latter at higher temperatures:

$$2C^6H^7N + NO^2H = C^{12}H^{11}N^3 + 2H^2O.$$

Diazo-amidobenzene or azodiphenyldiamine is described at p. 460, vol. iv. Amidodiphenylimide is identical with a yellow substance which Schiff obtained (*Compt. rend.* lvi. 1234) by the action of stannate or antimonate of sodium on a salt of aniline. It may be prepared by heating to 100°, 10 pts. of water, 1 part of aniline nitrate, and 3 pts. of sodium stannate, then gradually adding caustic soda. A brisk reaction is thereby set up, and the operation may be regarded as terminated when the liquid assumes a red colour on being mixed with an acid. It is then left to cool, the stannic oxide is removed by means of hydrochloric acid, and the residue is purified by repeated solution in dilute boiling hydrochloric acid and precipitation with ammonia.

Amidodiphenylimide is a yellow crystalline powder. All its solutions when slightly acidulated dye silk and wool of a deep lemon-yellow colour. The picrate dies wool with a colour approaching to cochineal-red. Heated with aniline it yields a blue dye. A very remarkable circumstance connected with these isomeric aniline yellows is that they are volatile and may be removed from tissues by the mere application of heat (Martius a. Griess, *Bull. Soc. Chim.* 1866 [2] vi. 158).

Toluidine treated with nitrous acid or with sodium stannate yields a compound homologous with amidodiphenylimide (Martius a. Gries).

Jacobsen (*Deutsche Industrie-Zeitung*, 1866, p. 458) produces a yellow colouring matter by mixing 100 pts. of aniline hydrochloride with 400 pts. of water and 40 pts. of mercurous nitrate. After 24 hours, the mass is redissolved in boiling water, which on cooling deposits the product in a state of purity.

Zinaline.—This name is given by Vogel (*J. pr. Chem.* xciv. 453) to a yellow colouring matter which he obtains by the action of nitrous acid on aniline, or on any of the colouring matters derived from it. It is described as a substance having a fine yellow colour, insoluble in water, soluble in alcohol, ether, chloroform, acids, and alkalis. The alkaline solution has a splendid red colour, and on addition of acid deposits the zinaline with its original yellow tint. Zinaline is moderately stable, not being altered by oxidising agents or by sulphurous acid. It melts below 100°, and at a higher temperature gives off thick yellow vapours, then suddenly takes fire with a slight detonation. Vogel assigns to it the formula $C^{20}H^{19}N^2O^6$.

USES OF ANILINE COLOURS.—1. *In Dyeing and Calico-printing.*—The aniline colours are mostly organic bases or salts, and thereby differ essentially from most of the vegetable colouring matters, which are weak acids. Hence considerable difficulty was at first found in their application to dyeing and printing, because they would not combine with the ordinary mordants used for the colouring matter of dye-woods, such as alumina and oxide of tin. These observations refer to the dyeing and printing of vegetable fibres, and not to silk or wool, as these materials absorb the aniline colours without the intervention of a mordant.

In silk-dyeing the principal difficulty experienced in applying these colours was owing to their great affinity for the fibre, which interferes with the production of an even colour, especially in dyeing light shades. After a time, however, it was found that this obstacle could be overcome by dyeing the silk in a weak soap-lather to which the colour had been added. This not only caused the dyeing to proceed with less rapidity, but also kept the face of the silk in good condition. Silk dyed by this process is left soft, but may afterwards be rendered hard or 'scroop' by rinsing in a bath of slightly acidulated water. This process was first used for dyeing silk with the mauve or aniline purple. It has, however, been since found suitable for nearly all the aniline colours, as magenta, Hofmann and Britannia violets, &c.

The process of *printing* silk with aniline colours is comparatively simple. An aqueous or alcoholic solution of the colouring matter is thickened with gum senegal, printed on with blocks, and when dry, exposed to the action of steam for about half an hour. The gum is then washed off, and the goods are finished.

A *discharge style* may be produced on silk dyed with magenta by printing on it with powdered zinc mixed with gum. The rosaniline, $C^{20}H^{19}N^3$, is thereby converted into leucaniline, $C^{20}H^{21}N^3$, the compounds of which are white. The same process may be applied to any of the coloured derivatives of magenta. Two colours may in like manner be produced on silk (for example, a green ground with purple spots) by taking silk dyed with any of the derivatives of magenta, and printing it with the discharge previously mixed with the colour it is desired to introduce, of course employing a colouring matter which is not affected by the discharge, as aniline purple, aniline pink, &c.

The dyeing of wool with aniline colours is a very simple process, the wool being merely worked in a hot aqueous solution of the desired colouring matter, no mordant being required. Acids are generally found to be injurious, and therefore a neutral bath is preferred, the operation being finished by bringing the temperature nearly up to that of boiling water. With *Nicholson's blue*, the process of dyeing is different, and consists of two distinct operations, the wool being first worked in an alkaline solution of the colour, which gives it a kind of grey or slate shade, and then in an acid bath, which develops the colour.

The *printing* of wool is similar to that of silk, the colouring matter being simply thickened with gum, printed on the goods, steamed, and then washed.

For dyeing cotton, mordants are required. The ordinary mordants, such as alum, are of no use, for the reason above mentioned. The method devised by Perkin and Pullar, depending upon the insolubility of the compounds which these colours form with tannin, is described, with reference to aniline purple, in the article DYEING (ii. 357). The cotton is first soaked in a decoction of sumach or other tanning agent, then in a solution of sodium stannate, and lastly in water acidulated with sulphuric acid. The cotton thus prepared contains an insoluble compound of tin and tannin, which possesses a great affinity for aniline purple and nearly all the other aniline colours.

For *printing* calico with aniline colours, the method now almost universally employed is that of Perkin and Schultz, which consists in printing the colouring matter with a mordant composed of a solution of aluminium arsenite in aluminium acetate. On steaming the cloth printed with this mixture for about half an hour, the colour is firmly fixed in the fibre. After steaming, the goods are generally soaped and then finished. One of the great advantages of this process is that it can be worked in patterns with a great variety of colours; it is also suitable for nearly all the aniline colours as well as the mauve, yielding shades of great brilliancy.

The application of *aniline black* to calico-printing has been already noticed (p. 160; also iv. 456).

Other uses of Aniline Colours.—Although the chief use of these colours is for dyeing and calico-printing, they are, nevertheless, employed in the form of lakes in several other branches of industry, as in lithography, type-printing, paper-staining, &c. These lakes are usually prepared by adding to the solution of the colouring matter mixed with alum, a certain quantity of tannin or benzoic acid, which forms therewith an insoluble compound; some manufacturers likewise add soap.

The lakes thus prepared are now used to a large extent for paper-staining. They are likewise employed in lithography and type-printing; but for these latter purposes special preparations are more frequently used. Sometimes the lithographic ink or varnish is mixed with starch-powder stained with an alcoholic solution of the required aniline colour; sometimes the varnish is mixed with the dried precipitate obtained by adding water to a mixture of an aniline colour with an alcoholic solution of resin; sometimes again the base of the colouring matter is dissolved in oleic acid, whereby a mixture is obtained directly applicable to printing or lithography (*Dingler's polyt. J.* clxxx. 165).

Aniline dyes are likewise used for colouring a variety of objects, such as soaps, vinegars, and paraffin, for staining horn, ivory, &c. Methods of staining horn and wood with these colours are described by Stubenbach (*Bull. Soc. Chim.* [2] xi. 95).

The peculiar bronze surface produced by evaporating a solution of an aniline colour has been made available for giving such a bronze surface to various articles of dress, as bonnets, flowers, and feathers; when thus used, however, the colours require a fixing agent, otherwise a shower of rain will wash them out.

ANISAMIC ACID. See Amidanisic Acid (p. 172).

ANISE-CAMPHOR. See Anethol (p. 156).

ANISHUMIN. $C^{18}H^{14}O^3$.—A body formed, together with acetic acid and other products, by the action of acetyl chloride on anisic aldehyde:

$$2C^8H^8O^2 + C^2H^3OCl = HCl + 2H^2O + C^{18}H^{14}O^3.$$

The mixture heated to 150° for twenty-four hours yields a black mass, from which water and ammonia extract a small quantity of anisic acid. The anishumin, which is the chief product, is dark-coloured, insoluble in water, ammonia, soda-ley, alcohol, and ether (A. Rossel, *Zeitschr. f. Chem.* [2] v. 653).

ANISIC ACID. $C^8H^8O^3$.—Zervas (*Ann. Ch. Pharm.* ciii. 388) prepares this acid by oxidising anise oil with chromic acid, namely by adding 1 pt. of anise oil and 7 pts. of strong sulphuric acid to a solution of 6 pts. potassium dichromate in 9 pts. of water contained in a capacious vessel. When the action is over, cold water is added and the precipitated anisic acid, amounting to 50 p. c. of the oil, is crystallised from alcohol. Ladenburg (*ibid.* cxli. 241) pours 1 pt. of anise oil into a solution of 5 pts. potassium chromate in 10 pts. sulphuric acid and 20 pts. water, heated to 50°, filters the liquid when cold, and separates the anisic acid from the chrome-alum formed at the same time by solution in ammonia; it is then precipitated from the ammonium salt by hydrochloric acid. Anise oil thus treated yields from 55 to 75 p. c. anisic acid. Erdmann (*J. pr. Chem.* lxxi. 198) has obtained anisic acid (together with picric, oxalic, and hydrocyanic acids) by the oxidising action of warm nitric acid on carajuru or chica, the red colouring matter of *Bignonia Chica* (i. 747).

Anisic acid has the constitution of methyl-paraoxybenzoic acid, $C^7H^5(CH^3)O^3$ or $C^6H^4\left\{\begin{matrix}OCH^3\\COOH\end{matrix}\right.$, and may be converted into paraoxybenzoic acid by heating with concentrated hydriodic acid (iv. 353) or with hydrochloric acid (Graebe, *Ann. Ch. Pharm.* cxxxix. 134), iodide or chloride of methyl being formed at the same time: e.g.

$$C^8H^8O^3 + HCl = C^7H^6O^3 + CH^3Cl.$$

Conversely, paraoxybenzoic acid may be converted into anisic acid: *a.* By treating ethyl paraoxybenzoate, $C^7H^5(C^2H^5)O^3$ (a crystalline ether prepared by passing hydrochloric acid gas into an alcoholic solution of the acid, precipitating with water, drying over oil of vitriol, and distilling), with strong soda-ley, or adding sodium to its ethereal solution, whereby it is converted into sodium-ethyl paraoxybenzoate, $C^7H^4Na(C^2H^5)O^3$, and heating the alcoholic solution of this sodium-ether for a few hours to 110°–120° with methyl iodide. Ethyl anisate is then formed according to the equation:

$$\underset{\substack{\text{Sodium-ethyl}\\\text{Paraoxybenzoate.}}}{C^6H^4\left\{\begin{matrix}ONa\\CO^2C^2H^5\end{matrix}\right.} + CH^3I = NaI + \underset{\substack{\text{Ethyl}\\\text{Anisate.}}}{C^6H^4\left\{\begin{matrix}OCH^3\\CO^2C^2H^5\end{matrix}\right.}$$

From this ethylic ether the acid may be obtained in the usual way (Graebe, *loc. cit.*).

β. Monopotassic paraoxybenzoate, $C^7H^5KO^3$, obtained by neutralising the acid with the theoretical quantity of potassium carbonate, is converted into the dipotassic salt $C^7H^4K^2O^3$, by treatment with potassium hydrate; and this when treated with methyl iodide is converted into the methylic ether of methyl-paraoxybenzoic acid or methyl anisate:

$$\underset{\substack{\text{Dipotassic}\\\text{paraoxybenzoate.}}}{C^6H^4\left\{\begin{matrix}OK\\CO^2K\end{matrix}\right.} + 2CH^3I = 2KI + \underset{\substack{\text{Methyl}\\\text{anisate.}}}{C^6H^4\left\{\begin{matrix}OCH^3\\CO^2CH^3\end{matrix}\right.}$$

To prepare this ether, the calculated quantities of monopotassic paraoxybenzoate, potassium hydrate, and methyl iodide are heated together in a sealed tube to 120°. On treating the contents of the tube with water, the methyl anisate separates as an oil which dissolves in ether, and separates therefrom in the crystalline form. This ether boiled for a long time with strong potash-ley, dissolves and forms potassium anisate, from which anisic acid (melting at 175°) may be separated by hydrochloric acid. By using ethyl iodide instead of methyl iodide in the above reaction, and proceeding in the same way, ethylparaoxybenzoic acid, $C^7H^5(C^2H^5)O^3$, the next higher homologue of anisic acid, may be obtained (Ladenburg, *Ann. Ch. Pharm.* cxli. 241; *Jahresb.* 1866, p. 388). See PARAOXYBENZOIC ACID in this volume.

γ. Anisic acid is also produced by the oxidation of the methylic ether of cresol, $C^6H^4(OCH^3).CH^3$. This ether is prepared by treating cresol with methylic iodide and a little methyl alcohol in an apparatus so arranged that the condensed vapours may flow back again, the vessel being plunged into cold water if the action becomes too violent, afterwards gently heated, and the product washed with water and caustic potash, then purified by distillation. The colourless liquid thus obtained, boiling at 174°, is converted into anisic acid by heating it with potassium dichromate and sulphuric acid in a flask with upright condensing tube (Körner, *Bull. Soc. Chim.* [2] x. 468.)

Anisates. (Engelhardt, *J. pr. Chem.* xxiv. 417.)—Anisic acid is monobasic, the formulæ of its salts being $M'C^8H^7O^3$ for univalent and $M''(C^8H^7O^3)^2$ for bivalent metals. Anisates corresponding to the bimetallic or so-called basic salicylates (v. 154) have not been obtained, excepting in the case of the lead-salt. The *potassium salt* $KC^8H^7O^3$ crystallises from alcohol of 70 p. c. in thin nacreous laminæ. The similarly prepared *sodium salt* forms shining transparent rhombic laminæ, $2NaC^8H^7O^3.H^2O$, which, by prolonged contact with the mother-liquor, are converted into efflorescent, apparently monoclinic crystals, containing $NaC^8H^7O^3.5H^2O$. The *barium salt* $Ba''(C^8H^7O^3)^2$ crystallises in thick, colourless, shining rhombic plates; the *strontium salt* $Sr''(C^8H^7O^3)^2.H^2O$, and the calcium salt $Ca''(C^8H^7O^3)^2.H^2O$, in laminæ which give off their water at 140°–170°. The *magnesium salt* $Mg''(C^8H^7O^3)^2.4H^2O$ dissolves easily in water and in alcohol, and crystallises from the latter in stellate groups of flexible needles. The *normal lead salt* $Pb''(C^8H^7O^3)^2.H^2O$ is obtained by precipitating ammonium anisate with lead-acetate, as a heavy white powder, which crystallises from hot water in shining laminæ, fusing, with loss of water, between 80° and 90°. A boiling solution of this salt yields with basic lead acetate, a salt containing $2Pb''C^8H^6O^3.H^2O$, which becomes anhydrous at 140°. The greenish blue precipitate thrown down by anisate of sodium or ammonium from a *cupric salt* is a mixture of anisic acid with a basic salt (Zervas). According to Schiff (*Jahresb.* 1862, p. 204), a blackish-green *diammocupriconium anisate*, $(N^2Cu''Am^2H^4)(C^8H^7O^3)^2.2H^2O$, is obtained by dissolving cupric anisate in ammonia and leaving the solution to evaporate in an atmosphere of ammonia.

NITRANISATES.—The *potassium salt* $KC^8H^6(NO^2)O^3.H^2O$ crystallises from alcohol in shining elongated tables; the *sodium salt* $NaC^8H^6(NO^2)O^3.H^2O$, from water and alcohol, in yellow needles; the *barium salt* $Ba''[C^8H^6(NO^2)O^3]^2.4H^2O$, and the *strontium salt* $Sr''[C^8H^6(NO^2)O^3]^2.H^2O$, are white flocculent precipitates; the *calcium salt* $Ca''[C^8H^6(NO^2)O^3]^2.4H^2O$ when re-crystallised from water forms microscopic flexible needles. The *lead salt* $Pb''[C^8H^6(NO^2)O^3]^2$ crystallises in needles which explode violently at a red heat (Engelhardt, *loc. cit.*).

Amidanisic Acid, $C^8H^7(NH^2)O^3 = C^6H^3(NH^2)\left\{\begin{matrix}OCH^3\\CO^2H\end{matrix}\right.$, or *Oxyanisamic acid*, $\left.\begin{matrix}H^2\\(C^8H^5O)'''\\H^2\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}$, improperly called *Anisamic acid* (i. 296).—This acid, like other amidated acids, forms crystalline compounds with mineral acids. With *hydrochloric acid* it forms the compound $C^8H^9NO^3.HCl$, which crystallises in slender white needles moderately soluble in water and in boiling alcohol, sparingly soluble in dilute aqueous hydrochloric acid. This hydrochloride forms with *platinic chloride* a double salt, $2(C^8H^9NO^3.HCl).PtCl^4$, which crystallises in golden-yellow needles easily soluble in warm alcohol and water. With *nitric acid*, amidanisic acid forms the compound $C^8H^9NO^3.HNO^3$, easily soluble in hot water and alcohol, sparingly soluble in nitric acid, and crystallising therefrom in tufts of prisms. With *sulphuric acid* it forms the compound $2C^8H^9NO^3.H^2SO^4$, which has a saccharine taste, dissolves easily in water, and crystallises from alcohol in silky needles (Cahours, *Ann. Ch. Phys.* [3] liii. 322).

Amidanisic acid distilled with excess of caustic *baryta* or *potash* is decomposed, with formation of anisidine, $C^7H^9NO^2$ (Cahours). Dissolved in excess of nitric acid and subjected to the action of *nitrogen dioxide*, it is converted, with evolution of nitrogen, into a crystalline non-azotised acid (Cahours). By the action of *nitrous* *acid* or a *nitrous ether*, not in excess, on its cold alcoholic solution, it is converted into diazoanis-amidanisic acid. $C^{16}H^{15}N^3O^6 = C^8H^6N^2O^3.C^8H^9NO^3$ (Griess; see iv. 289):

$$2C^8H^9NO^3 + HNO^2 = C^{16}H^{15}N^3O^6 + 2H^2O.$$

Amidanisic Ethers.—The *ethylic ether* $C^8H^8(C^2H^5)NO^3$ is produced by the action of ammonium sulphide on an alcoholic solution of ethyl nitranisate (i. 302). The solution, concentrated by gentle heat, and filtered from separated sulphur, yields ethyl amidanisate, on further evaporation, as an oil which crystallises after some time, and may be obtained by repeated crystallisation in colourless prisms easily soluble in warm alcohol, less soluble in ether. It dissolves easily in aqueous alkalis and forms crystalline compounds with acids. The *hydrochloride* $C^8H^8(C^2H^5)NO^3.HCl$ forms crystals soluble in alcohol and ether, colourless after recrystallisation; the *platinochloride* $2[C^8H^8(C^2H^5)NO^3.HCl].PtCl^4$ separates from alcoholic solution in brownish-red prisms, which become dull on exposure to the air, and are insoluble in ether.

Methyl Amidanisate, $C^8H^8(CH^3)NO^3$, is prepared like the ethyl compound, which it resembles. Its *hydrochloride* crystallises in small shining prisms, and unites with platinic chloride, forming the compound $2[C^8H^8(CH^3)NO^3.HCl].PtCl^4$, which crystallises from alcohol in reddish prisms (Cahours, *loc. cit.*).

Azo-anisic acid, $C^{16}H^{14}N^2O^6$, is produced by the action of sodium-amalgam on an alkaline solution of nitranisic acid, acidulated towards the end of the reaction. A coloured substance is thereby produced, the ammoniacal solution of which deposits, on addition of barium chloride, a small quantity of a red barium salt, and afterwards, in a closed vessel, yellow crystals of *barium azoanisate*, $C^{16}H^{12}BaN^2O^6$. The acid separated from this barium salt is yellowish, insoluble in water, alcohol, and ether, and does not reduce silver solutions (Alexejeff, *Compt. rend.* lv. 478; Strecker, *Jahresb.* 1863, p. 347).

Chloranisic and **Bromanisic Acids** (Reinecke, *Bull. Soc. Chim.* [2] vii. 177).—The monochlorinated and monobrominated acids, produced by the action of aqueous chlorine and bromine on anisic acid, are described in vol. i. 801, 302.

Dichloranisic acid, $C^8H^6Cl^2O$, is produced, together with tetrachloroquinone, by treating anisic acid with hydrochloric acid and potassium chlorate in presence of a large quantity of water. It crystallises from alcohol in large shining needles, insoluble in water, melting at 196°.

Dibromanisic acid, $C^8H^6Br^2O^3$, is produced by heating anisic acid with bromine and water to 120°. It resembles the dichlorinated acid, melts at 207°–208°, and sublimes in long beautiful needles.

Both these acids dissolve without decomposition in hot nitric acid, and are deposited therefrom on cooling; the monochlorinated and monobrominated acids are easily decomposed under the same circumstances, with loss of CO^2; a similar decomposition of the dichlorinated and dibrominated acids takes place only after long boiling.

Dibromanisic acid subjected to the prolonged action of bromine and water, is converted into tribromanisol, according to the equation:

$$C^8H^6Br^2O^3 + Br^2 = C^7H^5Br^3O + CO^2 + HBr.$$

Tribromanisol crystallises from boiling alcohol in colourless needles, which melt at 87°, and may be sublimed. Bromine converts it into tetrabromoquinone, $C^6Br^4O^2$, doubtless with simultaneous formation of methyl bromide.

Iodanisic Acid. $C^8H^7IO^3$.—Griess obtained this acid, together with the hydriodate of amidanisic acid, by the action of hydriodic acid on diazo-amidanisic acid (*Ann. Ch. Pharm.* cxvii. 1). It is also produced (probably in a different modification) by the action of iodine and iodic acid on anisic acid (Peltzer, *Bull. Soc. Chim.* [2] ix. 148):

$$5C^8H^8O^3 + HIO^3 + 2I^2 = 5C^8H^7IO^3 + 3H^2O.$$

The materials, in the proportions indicated by the equation, are heated together for about six hours to 115°–150°. The acid is nearly insoluble in water, whether hot or cold; dissolves in 165 pts. of cold ether, and is somewhat more soluble in boiling ether and alcohol. The solutions deposit the acid in needle-shaped crystals having a vitreous lustre. It melts at 234·5°, and sublimes at a somewhat lower temperature in small nacreous laminæ. Nascent hydrogen converts it into anisic acid.

Ammonium iodanisate forms small groups of hard, white, needle-shaped crystals which give off ammonia at 100°. The *barium salt* $Ba(C^8H^6IO^3)^2.3H^2O$ forms vitreous prisms several lines long. The *calcium salt* $Ca(C^8H^6IO^3)^2.3H^2O$ is more soluble than the barium salt, and crystallises in small nacreous needles. The *lead salt* is a white curdy precipitate, soluble in boiling water, and crystallising therefrom in anhydrous, microscopic, fusible laminæ (Peltzer).

Acid $C^9H^{10}O^3$, homologous with Anisic Acid. This acid, isomeric with phloretic acid, is produced by boiling anisic cyanhydrin, $C^6H^4(OCH^3).CH^2CN$, with strong potash as long as ammonia is evolved, and treating the resulting solution with hydrochloric acid. The new acid then separates as an oily liquid, which dissolves in ether, and remains on evaporation as a yellowish oil, to be purified by solution in caustic soda, reprecipitation, and crystallisation from water. It then forms nacreous laminæ, melting between 85° and 86°, easily soluble in alcohol, ether, and boiling water, very slightly soluble in cold water. By decomposing the easily soluble sodium salt with silver nitrate, the silver salt $C^9H^9AgO^3$ is obtained as a precipitate, very slightly soluble in cold, more soluble in boiling water (Cannizzaro, *Ann. Ch. Pharm.* cxvii. 243).

ANISIC ALCOHOL. $C^8H^{10}O^2$.—This alcohol, though it contains two atoms of oxygen, does not exhibit the properties of a diatomic alcohol, having only one atom of hydrogen replaceable by alcoholic or acid radicles. It is, in fact, the alcohol corresponding to anisic or methyl-paraoxybenzoic acid, and is represented by the formula

$$C^6H^4\left\{\begin{matrix}OCH^3\\CH^2OH,\end{matrix}\right.$$

which evidently contains only one atom of typic hydrogen. When treated with hydrochloric acid, it exchanges the group OH for Cl, and is converted into anisic chlorhydrin, C^8H^9OCl or $C^6H^4\left\{\begin{matrix}OCH^3\\CH^2Cl\end{matrix}\right.$; and this compound heated to 100° for several days with an equivalent quantity of sodium methylate and an excess of methyl alcohol, is converted into the methylic ether of anisic alcohol, $C^9H^{12}O^2$ or $C^6H^4\left\{\begin{matrix}OCH^3\\CH^2OCH^3.\end{matrix}\right.$ On filtering from the sodium chloride formed at the same time, evaporating, adding water, dissolving the oil thereby separated in absolute alcohol, and rectifying, this ether is obtained as a colourless liquid, boiling constantly and without decomposition at 225·5° under a barometric pressure of 758 mm. (Cannizzaro, *Ann. Ch. Pharm.* cxxxvii. 244).

The methylic ether of anisic alcohol is isomeric with the dimethylic ether of benzylic glycol, $C^6H^5.CH(OCH^3)^2$, obtained by heating dichlorotoluene, $C^7H^6Cl^2$, or the isomeric compound called chlorobenzol, $C^6H^5.CHCl^2$, to 100°, with an equivalent quantity of sodium methylate. The product thus obtained does not exhibit a constant boiling point, but its properties are quite distinct from those of the methylic ether of anisic alcohol, inasmuch as when heated to 100° with strong acetic acid, it is resolved into methyl acetate and benzoic aldehyde (bitter almond oil):

$$\underset{\substack{\text{Dimethylic}\\\text{benzyl glycol.}}}{C^6H^5.CH(OCH^3)^2} + \underset{\text{Acetic acid.}}{2C^2H^3O(OH)} = \underset{\text{Methyl acetate.}}{2C^2H^3O(OCH^3)} + \underset{\substack{\text{Benzoic}\\\text{aldehyde.}}}{C^6H^5.CHO} + H^2O;$$

whereas methyl-anisic ether treated in like manner does not yield a trace of benzoic aldehyde (Cannizzaro, *Ann. Ch. Pharm.* cxxxvii. 244).

ANISIC ALDEHYDE. $C^8H^8O^2$ (i. 307).—A. Rossel (*Ann. Ch. Pharm.* cli. 25) prepares this compound by oxidising anise oil with chromic acid: 300 grms. strong sulphuric acid and 850 grms. water are poured upon 200 grms. potassium dichromate in a capacious flask; 100 grms. of anise oil are added after the liquid has completely cooled; and the whole is vigorously shaken, the temperature of the mixture rising to 70°–80°. When the reaction is complete, the liquid is diluted with water to 1½ time its volume, and distilled, warm water being added through a funnel-tube to replace that which distils off. In this manner a quantity of anisic aldehyde is obtained equal to 50 p. c. of the oil of anise used, together with 10 p. c. anisic acid.

Pure anisic aldehyde does not become dark-coloured by keeping; it boils at 247°–248°, under a pressure of 733·5 mm. (?), has a density of 1·228 at 18°, and dissolves in strong sulphuric acid with a colour of carmine, turning to violet on heating (Rossel). For the action of sodium amalgam, see the next page.

ANISIC CHLORHYDRIN. $C^6H^4(OCH^3).CH^2Cl$. — See ANISIC ALCOHOL.

ANISIC CYANHYDRIN. $C^9H^9NO = C^6H^4(OCH^3).CH^2CN$.—Obtained as a brown oil, by heating an alcoholic solution of anisic chlorhydrin with potassium cyanide, distilling off the alcohol from the filtered liquid, mixing the residue with *acid* or a *nitrous ether*, not in excess, on its cold alcoholic solution, it is converted into diazoanis-amidanisic acid. $C^{16}H^{15}N^3O^6 = C^8H^6N^2O^3.C^8H^9NO^3$ (Griess; see iv. 289):

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Chloranisic and **Bromanisic Acids** (Reinecke, *Bull. Soc. Chim.* [2] vii. 177).—The monochlorinated and monobrominated acids, produced by the action of aqueous chlorine and bromine on anisic acid, are described in vol. i. 301, 302.

Dichloranisic acid, $C^8H^6Cl^2O$, is produced, together with tetrachloroquinone, by treating anisic acid with hydrochloric acid and potassium chlorate in presence of a large quantity of water. It crystallises from alcohol in large shining needles, insoluble in water, melting at 196°.

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$$5C^8H^8O^3 + HIO^3 + 2I^2 = 5C^8H^7IO^3 + 3H^2O.$$

The materials, in the proportions indicated by the equation, are heated together for about six hours to 115°–150°. The acid is nearly insoluble in water, whether hot or cold; dissolves in 165 pts. of cold ether, and is somewhat more soluble in boiling ether and alcohol. The solutions deposit the acid in needle-shaped crystals having a vitreous lustre. It melts at 234·5°, and sublimes at a somewhat lower temperature in small nacreous laminæ. Nascent hydrogen converts it into anisic acid.

Ammonium iodanisate forms small groups of hard, white, needle-shaped crystals which give off ammonia at 100°. The *barium salt* $Ba(C^8H^6IO^3)^2.3H^2O$ forms vitreous prisms several lines long. The *calcium salt* $Ca(C^8H^6IO^3)^2.3H^2O$ is more soluble than the barium salt, and crystallises in small nacreous needles. The *lead salt* is a prolonged heating of purified anise-oil with potassium hydrate. On adding water to the product, a small quantity of unaltered anethol separates as an oil, while potassium anolate remains in solution; and on decomposing this solution with an acid, carefully avoiding rise of temperature, anol separates in yellow flocks, which crystallise from hot water in white shining laminæ. Anol melts at 92·5°, boils at about 250°, and dissolves in alcohol, ether, and chloroform; it does not, however, always crystallise from these solutions, but sometimes passes, especially on exposure to the air, into a brown liquid insoluble in hot water (Ladenburg, *Deut. Chem. Gesellsch.* 1869, p. 371; *Zeitschr. f. Chem.* [2] v. 575).

ANTHRACENE. $C^{14}H^{10}$ (Berthelot, *Bull. Soc. Chim.* [2] vii. 223; viii. 238; ix. 295.—Graebe a. Liebermann, *Zeitschr. f. Chem.* [2] iv. 279, 503, 724; v. 602; vi. 257; *Ann. Ch. Pharm. Suppl.* vii. 257.—Fritzsche, *N. Petersb. Acad. Bull.* xi. 385; xiii. 531; *Jahresb.* 1867, p. 600; 1868, p. 433).—The name anthracene has been applied to two different hydrocarbons, viz. the compound $C^{14}H^{10}$, examined by Fritzsche and Anderson, described in vol. iv. pp. 850–852 (as paranaphthalene), and the compound $C^{15}H^{12}$, examined by Dumas a. Laurent (*Ann. Ch. Phys.* [2] l. 187), first called paranaphthalene, and afterwards by Laurent, anthracene. Berthelot regards this last compound as methyl-anthracene. Graebe a. Liebermann have, however, shown that the analyses which Dumas a. Laurent gave of their hydrocarbon are not sufficiently exact to decide between the formulæ $C^{15}H^{12}$ and $C^{14}H^{10}$; that, on the other hand, the analyses of Laurent's *anthracenuse* agree very well with the formula $C^{14}H^{8}O^{2}$, and not at all with Laurent's own formula, $C^{15}H^{9}O^{2}$. The so-called anthracenuse is therefore identical with the compound called by Anderson *oxanthracene*, by Graebe a. Liebermann *anthraquinone*, and appears to have been obtained from a mixture of hydrocarbons consisting mainly of $C^{14}H^{10}$. It may be concluded therefore that the hydrocarbon $C^{15}H^{12}$ has no existence, at least as a constituent of coal-tar. Fritzsche's *photene* is identical with pure anthracene, $C^{14}H^{10}$.

The preparation of anthracene from coal-tar, according to Anderson and Fritzsche, is given in vol. iv. p. 850. Fritzsche's latest method is as follows: Crude anthracene is dissolved in hot coal-tar naphtha, and the less fusible portion which separates out each time is repeatedly crystallised till it exhibits the crystalline characters to be presently described. The yellow colour, arising from chrysogen, which obstinately adheres to it, may be removed by exposure to sunshine. Lastly, the hydrocarbon must be boiled with alcoholic picric acid, to remove any possible trace of a more soluble hydrocarbon of higher boiling point. Berthelot rectifies the solid product of the distillation of coal-tar, collecting apart that which passes over from 340° to a little above the boiling point of mercury; distils again, arresting the operation at 350°; dissolves the residue in boiling coal-oil (B. P. 120°–150°); presses the crystals which are deposited from the solution on cooling; and repeats this operation four or five times. The product is then recrystallised from alcohol, and the purification is finally completed by cautious sublimation in an ordinary retort.

Anthracene may be formed artificially: 1. By heating benzyl chloride, C^7H^7Cl, with water to 200°, dibenzyl, $C^{14}H^{14}$, being probably formed at the same time according to the equation,

$$4C^7H^7Cl = C^{14}H^{10} + C^{14}H^{14} + 4HCl$$

(Limpricht, *Ann. Ch. Pharm.* cxxxix. 303; *Jahresb.* 1866, p. 592).—2. By passing the vapour of toluene or xylene through a red-hot tube:

$$\underset{\text{Xylene.}}{3C^8H^{10}} - 3H^2 = \underset{\text{Toluene.}}{2C^7H^8} + \underset{\text{Naphthalene.}}{C^{10}H^8}$$

$$\underset{\text{Toluene.}}{2C^7H^8} - 3H^2 = \underset{\text{Anthracene.}}{C^{14}H^{10}}$$

3. By passing a mixture of benzene and ethylene gas or cinnamene vapour, or of diphenyl or chrysene vapour with ethylene gas, through a red-hot tube; also by exposing a mixture of benzene and naphthalene to a white heat (Berthelot):

$$\underset{\text{Benzene.}}{2C^6H^6} + \underset{\text{Ethylene.}}{C^2H^4} = 3H^2 + C^{14}H^{10}$$

$$\underset{\text{Benzene.}}{C^6H^6} + \underset{\text{Cinnamene.}}{C^8H^8} = 2H^2 + C^{14}H^{10}$$

$$\underset{\text{Diphenyl.}}{C^{12}H^{10}} + \underset{\text{Ethylene.}}{C^2H^4} = 2H^2 + C^{14}H^{10}$$

$$\underset{\text{Chrysene.}}{C^{18}H^{12}} + \underset{\text{Ethylene.}}{C^2H^4} = C^6H^6 + C^{14}H^{10}$$

$$\underset{\text{Naphthalene.}}{C^{10}H^8} + \underset{\text{Benzene.}}{3C^6H^6} = 3H^2 + 2C^{14}H^{10}$$

4. By heating alizarin with zinc-dust—a mixture of metallic zinc, zinc-oxide, and zinc hydrate—the hydrogen required for the transformation being supplied by the hydrate:

$$C^{14}H^8O^4 + H^2 + Zn^4 = 4ZnO + C^{14}H^{10}.$$

A mixture of 1 pt. alizarin and 30 to 50 pts. of good zinc-dust is placed at the closed end of a combustion-tube, a layer of zinc-dust several inches long being placed in front of it and about 6 inches of the tube being left empty; the unmixed zinc-dust is then heated, and afterwards the mixture is gradually heated to low redness. The quantity of anthracene thus obtained is about 30 per cent. of the alizarin used, the calculated quantity being 74 per cent. The loss arises from the formation of secondary products. Anthracene may be obtained in like manner from purpurin, $C^{14}H^8O^5$; chrysophanic acid, $C^{14}H^8O^4$ or $C^{14}H^{10}O^4$; and aloïn (Graebe a. Liebermann).

Anthracene crystallises in well-defined four- or six-sided tables having a dazzling white lustre and a beautiful violet fluorescence, which however is exhibited only when the crystals are quite pure and white (Fritzsche; see also Perkin, *Chem. Soc. J.* [2] ix. 22). From large quantities of the alcoholic solution, still coloured yellow by chrysogen, it separates in monoclinic crystals exhibiting the combination oP . ∞P . + P . + 2P∞, and having their axes a (clinod.) : b : c (principal) = 1·422 : 1 : 1·878 (Fritzsche). It melts at 210°–212° (Fritzsche), at 213° and distils at about 360° (Graebe a. Liebermann). By prolonged exposure to *light* it is converted into an isomeric body, paranthracene (paraphotene), which forms microscopic flat crystals, or four-sided tables, melting at 244°, nearly insoluble in all solvents, not attacked by strong sulphuric acid, by ordinary nitric acid even at the boiling heat, by bromine at 100°, or by a solution of bromine in carbon bisulphide; reconverted into anthracene by fusion.

Anthracene heated to 280° with 100 times its weight of strong *hydriodic acid* is transformed into several hydrocarbons of the paraffin series C^nH^{2n+2}, viz. tetradecane, $C^{14}H^{30}$, as principal product; septane, C^7H^{16}, in considerable quantity; sextane, C^6H^{14}, and ethane, C^2H^6, in smaller quantity; also a somewhat considerable quantity of an oily, nearly solid paraffin, probably $C^{28}H^{58}$, which does not distil over at 300°. The formation of the first two and the last of these products is represented by the equations

$$C^{14}H^{10} + 20HI = C^{14}H^{30} + 10I^2; \quad C^{14}H^{10} + 22HI = 2C^7H^{16} + 11I^2;$$
$$2C^{14}H^{10} + 38HI = C^{28}H^{58} + 19I^2;$$

while the sextane and ethane are formed thus:

$$C^{14}H^{10} + 24HI = 2C^6H^{14} + C^2H^6 + 12I^2.$$

With a smaller quantity of hydriodic acid (20 times the weight of the anthracene), the principal product is toluene:

$$C^{14}H^{10} + 6HI = 2C^7H^8 + 3I^2,$$

with traces of benzene and ethane:

$$C^{14}H^{10} + 8HI = 2C^6H^6 + C^2H^6 + 4I^2;$$

and a small quantity of a liquid hydrocarbon volatising above 260°, apparently a hydride of anthracene:

$$C^{14}H^{10} + 2HI = C^{14}H^{12} + I^2.$$

Anthracene is converted by *oxidising agents*, as by a mixture of potassium dichromate and sulphuric acid, into anthraquinone, $C^{14}H^8O^2$, identical with Anderson's oxanthracene (iv. 352).

Respecting the conversion of anthracene into alizarin, $C^{14}H^8O^4$, see ALIZARIN (p. 83).

Anthracene Hydrides. The *dihydride* $C^{14}H^{12}$ is formed by heating anthracene to 150°–160° with hydriodic acid and red phosphorus; also by gradually adding sodium amalgam to anthracene gently warmed with alcohol of 95 per cent. in a flask with upright condenser, and neutralising the product from time to time with an acid till a sample of the product melts at 106°, or no longer turns red when heated with picric acid and benzol. It melts at 106°, sublimes at about the same temperature, boils without decomposition at 305°, crystallises in tabular monoclinic combinations oP . ∞P . −P∞; has a peculiar odour, especially strong when the substance is heated; is insoluble in water, but dissolves very abundantly in alcohol, ether, and benzol; distils with vapour of water or alcohol; does not fluoresce in the solid state, but its solutions exhibit a blue fluorescence. Strong *sulphuric acid* at 100° converts it into anthracene:

$$C^{14}H^{12} + SO^4H^2 = C^{14}H^{10} + 2H^2O + SO^2,$$

sulpho-acids of anthracene being formed as secondary products. *Bromine* added to a solution of the dihydride in carbon bisulphide produces dibromanthracene:

$$C^{14}H^{12} + 3Br^2 = C^{14}H^8Br^2 + 4HBr.$$

With less than 3 mol. bromine to 1 mol. of the dihydride, part of the latter remains unaltered, no reproduction of anthracene taking place. The dihydride heated with dilute *nitric acid* yields a number of nitro-products, amongst which is dinitroanthraquinone (Fritzsche's reagent, p. 180). It is not altered by boiling with iodine in alcoholic solution, and not perceptibly altered by sodium amalgam (Graebe a. Liebermann).

The *hexhydride*, $C^{14}H^{16}$, is obtained by heating the dihydride to 200°–220° for ten or twelve hours with hydriodic acid and ¼ to ⅓ pts. by weight of amorphous phosphorus, washing the product with water, separating it from unaltered phosphorus by solution in alcohol, pressing the residue between bibulous paper, and distilling: the portion which boils at 290° is the hexhydride. It melts at 63°, dissolves easily in alcohol, ether, and benzol; crystallises therefrom in laminæ; is resolved at a red heat into hydrogen and anthracene; and is much less acted upon by nitric acid than the dihydride.

A *tetrahydride* of anthracene does not appear to exist; the dihydride treated with hydriodic acid alone is partly converted into hexhydride (Graebe a. Liebermann).*

Bromanthracenes. *Dibromanthracene*, $C^{14}H^8Br^2$, was first obtained by Anderson (iv. 351). Graebe a. Liebermann prepare it by treating anthracene under carbon bisulphide with 1 mol. bromine. It forms long yellow needles which melt at 221° (according to Anderson at 182°), dissolve easily in benzol, sparingly in alcohol and ether. With *picric acid* it forms a red crystalline compound; with sulphuric acid, a sulpho-acid. By nitric acid it is easily converted into anthraquinone. It is not altered by boiling with *potash*, either in alcoholic or in aqueous solution; but when heated with alcoholic potash to 160°–170°, it yields anthracene, together with aldehyde and acetic acid; probably thus:

$$C^{14}H^8Br^2 + 2KHO + C^2H^6O = C^{14}H^{10} + 2KBr + C^2H^4O^2 + H^2O.$$

Monobromanthracene does not appear to exist.

Dibromanthracene-tetrabromide, $C^{14}H^8Br^6$, is produced by spreading dibromanthracene (1 mol.) on a glass plate, and placing it under a bell-jar, together with a capsule containing the requisite quantity of bromine (2 mols.); washing the product, after complete absorption of the bromine, with ether; and recrystallising it from benzol: $C^{14}H^{10} + 4Br^2 = 2HBr + C^{14}H^8Br^2.Br^4$. Anderson obtained the same compound (iv. 352), but regarded it as anthracene-hexbromide, $C^{14}H^{10}Br^6$. It melts between 170° and 180° (at 182°, Anderson), and is at the same time resolved into tribromanthracene, bromine, and hydrobromic acid:

$$C^{14}H^8Br^6 = C^{14}H^7Br^3 + Br^2 + HBr.$$

Tribromanthracene, $C^{14}H^7Br^3$, obtained by heating the preceding compound to 200° as long as vapours of bromine and hydrobromic acid are given off, and crystallising the residue from benzol, forms yellow needles sparingly soluble in alcohol, easily in benzol, melts at 169°, and sublimes in needles. By *nitric acid* of sp. gr. 1·4, or, better, by *chromic acid* and glacial acetic acid, it is converted into dibromanthraquinone:

$$C^{14}H^7Br^3 + O^2 = Br^2 + C^{14}H^7BrO^2.$$

It unites directly with dry *bromine*, forming $C^{12}H^7Br^3.Br^4$ (Graebe a. Liebermann).

Tetrabromanthracene. $C^{14}H^6Br^4$ (obtained by Anderson, who regarded it as dibromanthracene dibromide, $C^{14}H^8Br^2.Br^2$).—Prepared by adding a strong aqueous solution of ¼ to ⅓ pt. potassium hydrate to 1 pt. dibromanthracene-tetrabromide heated with alcohol in the water-bath, and recrystallising the yellow product from commercial benzol of high boiling point. Melts at 254° (at 238°, Anderson), and is converted by oxidising agents, especially by nitric acid of sp. gr. 1·4 and potassium dichromate, into dibromanthraquinone (Graebe a. Liebermann).

Chloranthracenes. Anderson obtained the compounds $C^{14}H^{10}Cl^2$ and $C^{14}H^9Cl$ (iv. 353). *Dichloranthracene*, $C^{14}H^8Cl^2$, is formed by treating anthracene with chlorine at 100°, or by exposing it for some time to an atmosphere of chlorine at ordinary temperatures. It was obtained in the latter way by Laurent, who, however, assigned to it the incorrect formula $C^{15}H^8Cl^2$. Perkin (*Chem. Soc. J.* [2] ix. 14) prepares it by passing chlorine gas over benzol holding in suspension about one-fifth of its weight of purified commercial anthracene, until the whole becomes a crystalline pasty mass. The product is then thrown on a linen filter, drained, well washed with cold benzol, then dried, and further purified, first by distillation, then by two or three crystallisations from benzol. It then separates in golden-yellow needles. It dissolves easily in benzol, sparingly in alcohol and ether, melts at 205°, and sublimes in yellow needles. Its solutions, especially the alcoholic solution, exhibit a splendid blue fluorescence. It is not attacked by potash-ley. Oxidising agents convert it into anthraquinone. A mixture of the boiling solutions of dichloranthracene and picric acid in benzol yields on cooling, small bright red needles of dichloranthracene picrate, $C^{14}H^8Cl^2.C^6H^3(NO^2)^3O$ (Perkin).

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* Graebe a. Liebermann formerly stated that a tetrahydride was produced in this manner, but their more recent experiments show that the product was only a mixture.

Tetrachloranthracene, $C^{14}H^6Cl^4$, is prepared by passing chlorine over anthracene at 170°–180°, treating the product (probably dichloranthracene tetrachloride) with alcoholic potash, and crystallising the resulting yellow compound from benzol. Stellate groups of golden-yellow needles, slightly soluble in alcohol, somewhat more freely in hot benzol, nearly insoluble in cold benzol. Melts at 220°. Converted by nitric acid into dichloranthraquinone (Graebe a. Liebermann).

Sulpho-acids of Dichlor- and Dibrom-anthracene.

Disulpho-dichloranthracenic Acid. $C^{14}H^6Cl^2S^2O^6 = C^{14}H^6Cl^2\left\{\begin{matrix}SO^3H\\SO^3H\end{matrix}\right.$ (Perkins, *Chem. Soc. J.* [2] ix. 15).—Prepared by adding 1 pt. of dichloranthracene to about 5 pts. of fuming sulphuric acid, heating the mixture for a short time on the water-bath, then gradually pouring it into several times its bulk of water, neutralising with barium carbonate, and evaporating the filtrate to a small bulk. The sulpho-acid then remains as a slimy mass of minute orange-yellow needles, which may be drained on a porous tile. It is easily soluble in water; is precipitated therefrom by strong sulphuric or hydrochloric acid; has a strong acid taste and reaction. Its dilute solutions and those of its salts exhibit a strong blue fluorescence, less powerful, however, than that of a solution of æsculin. The composition of the acid is inferred from that of its salts.

The *sodium salt* $C^{14}H^6Cl^2(SO^3Na)^2$ crystallises in small orange-red needles easily soluble in water. The *barium salt* $C^{14}H^6Cl^2Ba(SO^3)^2$ is thrown down from the solution of the sodium salt by barium chloride, as a canary-yellow precipitate nearly insoluble in water. The *strontium salt* $C^{14}H^6Cl^2Sr(SO^3)^2$ separates on mixing the hot solutions of sodium disulphodichloranthracenate and strontium chloride, and evaporating, in yellow crusts, sparingly soluble in water. The *calcium salt* obtained by neutralisation is yellow and easily soluble in water.

Disulphodichloranthracenic acid subjected to the action of oxidising agents rapidly exchanges its chlorine for oxygen $(O^2)''$, and is converted into disulphanthraquinonic acid:

$$C^{14}H^6Cl^2(SO^3H)^2 + O^2 = C^{14}H^6(O^2)''(SO^3H)^2 + Cl^2.$$

A similar result is obtained by heating the chlorinated acid with strong sulphuric acid; thus:

$$C^{14}H^6Cl^2(SO^3H)^2 + SO^4H^2 = 2HCl + SO^2 + C^{14}H^6(O^2)''(SO^3H)^2.$$

Disulphodibromanthracenic Acid. $C^{14}H^6Br^2\left\{\begin{matrix}SO^3H\\SO^3H\end{matrix}\right.$ (Perkin, *Chem. Soc. J.* [2] ix. 19).—Prepared, like the preceding, by the action of fuming sulphuric acid on dibromanthracene. It is crystalline, and its dilute solutions are fluorescent, as also are those of its salts, but much less strongly than those of the dichlorinated acid. The *sodium salt*, obtained by adding sodium sulphate to the crude solution of the acid neutralised with barium carbonate, crystallises in easily soluble microscopic needles, containing $C^{14}H^6Br^2(SO^3Na)^2$. The *barium salt* $C^{14}H^6Br^2Ba(SO^3)^2$ obtained by precipitation is insoluble in water and in hydrochloric acid, even at the boiling heat.

Disulphodibromanthracenic acid is converted into disulphanthraquinonic acid by the action of oxidising agents, in the same manner as the dichlorinated acid. With strong sulphuric acid the reaction is

$$C^{14}H^6Br^2(SO^3H)^2 + 2SO^4H^2 = Br^2 + 2SO^2 + 2H^2O + C^{14}H^6(O^2)''(SO^3H)^2.$$

ANTHRACENE-CARBONIC ACID. $C^{14}H^9.CO^2H$ (Graebe a. Liebermann, *Deut. Chem. Ges. in Berlin*, 1869, 678; *Zeitschr. f. Chem.* [2] vi. 213).—Produced by melting anthracene with liquid carbonyl chloride (phosgene) in a sealed tube to 200° for twelve hours. On digesting the contents with dilute sodium carbonate, which leaves a resin undissolved, and acidulating the filtrate, anthracene-carbonic acid separates in light yellow flocks, consisting of interlaced needles. It is nearly insoluble in cold water, and but slightly soluble in boiling water, from which, however, it may be recrystallised. From alcohol, in which it dissolves easily at ordinary temperatures, it separates in long light-yellow needles having a silky lustre. In capillary tubes it melts at 206°, with evolution of carbon dioxide; but when a somewhat larger quantity is slowly heated in an oil-bath, it begins to decompose even at 150°, yielding a sublimate of anthracene. When heated with soda-lime, or more strongly by itself, it is completely resolved into anthracene and carbon dioxide. Its salts are decomposed by heat in a similar manner. They are mostly soluble in water and in alcohol. The *barium salt* is white; the *silver salt* $C^{14}H^9.CO^2Ag$ exhibits under the microscope the appearance of golden-yellow compressed prisms. The acid dissolved in glacial acetic acid is converted by oxidation with chromic acid into anthraquinone:

$$C^{14}H^9.CO^2H + O^3 = C^{14}H^8O^2 + H^2O + CO^2.$$

ANTHRAQUINONE. $C^{14}H^8(O^2)''$. Laurent's *Paranaphthalose* or *Anthracenuse*; Anderson's *Oxanthracene* (iv. 352); Fritzsche's *Oxyphotene.*—This compound, related to anthracene in the same manner as quinone, $C^6H^4O^2$, to benzene, is produced by oxidation of anthracene, and of its dichloro- and dibromo-derivatives. It is most easily prepared by dissolving anthracene in warm glacial acetic acid, adding 2 pts. by weight of potassium dichromate, and assisting the action, as soon as it slackens, by heating the liquid on the water-bath till the solution has acquired a deep green colour. On diluting with water, and distilling the separated well-washed and dried mass, anthraquinone passes over, while a cinder rich in chromium remains behind. For preparation on the small scale it is better to use as the oxidising agent a mixture of glacial acetic acid and chromic acid: there is then a less abundant formation of the products which carbonise during distillation (Graebe a. Liebermann; Fritzsche).

Anthraquinone melts at 273° and sublimes in yellow needles, sometimes in thick dark golden-yellow prisms. The yellow colour belongs essentially to it, but varies greatly in depth, according to the size of the crystals; finely divided anthraquinone, such as is obtained by precipitating a solution in sulphuric acid with water, appears nearly colourless. Anthraquinone is a very stable substance; it withstands the action of extremely energetic oxidising agents, and is not attacked by alcoholic potash at 200°, or even by fusion with potassium hydrate. *Bromine* does not act in the cold on anthraquinone either in the dry state or dissolved in carbon bisulphide; at 100° it forms dibromanthraquinone. When anthraquinone is heated to 150° for some hours with *hydriodic acid* (boiling at 127°) and a little yellow phosphorus, anthracene is produced, together with a small quantity of anthracene dihydride. Heated with excess of *zinc-dust*, it yields anthracene, the hydrogen necessary for the formation of that body being supplied by the zinc hydrate present:

$$C^{14}H^8O^2 + H^2 + Zn^2 = 2ZnO + C^{14}H^{10}.$$

Dibromanthraquinone, $C^{14}H^6Br^2O^2$, is obtained by heating an intimate mixture of anthraquinone and bromine to 100° for a considerable time. A better mode of preparation is to heat 1 pt. of tetrabromanthracene with 2 pts. potassium dichromate and 5 or 6 pts. colourless nitric acid of sp. gr. 1·4 in a capacious flask as long as bromine continues to escape; then dilute with water, and recrystallise the washed product from benzol. The oxidation succeeds well also with chromic acid and glacial acetic acid. Dibromanthraquinone crystallises in light-yellow needles, sublimes without decomposition, dissolves very slightly in alcohol, more easily in benzol and chloroform. By heating with potash it is converted into alizarin (p. 84).

Monobromanthraquinone, $C^{14}H^7BrO^2$, is obtained from tribromanthracene in the same manner as dibromanthraquinone from tetrabromanthracene. It crystallises in yellow needles, melts at 187°, sublimes without alteration, dissolves sparingly in alcohol, scarcely at all in cold benzol, with moderate facility in hot benzol. Heated with potassium hydrate it yields alizarin, according to the equation

$$C^{14}H^7BrO^2 + KHO + H^2O = C^{14}H^6(OH)^2O^2 + KBr + H^2.$$

Dichloranthraquinone, $C^{14}H^6Cl^2O^2$, is obtained, though not quite pure, by oxidation of tetrachloranthracene. It forms yellow needles, sparingly soluble in alcohol and ether, somewhat more soluble in benzol than the corresponding bromine compound.

Dinitro-anthraquinone, $C^{14}H^6(NO^2)^2O^2$, Anderson's *Dinitroxanthracene*, Fritzsche's *Oxydinitrophotene*, is obtained, together with anthraquinone, by heating anthracene to 90° with dilute nitric acid. The two bodies are separated by solution in boiling alcohol of 95 p. c., which on cooling deposits the nitro-compound in laminæ (Fritzsche, *N. Petersb. Acad. Bull.* xxii. 43; see also Anderson, iv. 352).*

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* Fritzsche's memoir contains voluminous directions for the preparation of this compound in the pure state; see also *Jahresb. f. Chem.* 1868, p. 395.

This compound, called 'Fritzsche's reagent,' unites directly with all the solid hydrocarbons of coal-tar, and is very useful for effecting their separation. By means of it Fritzsche has detected six different hydrocarbons in the mother-liquor of the preparation of anthracene. (See PHOSENE.) The compound of dinitro-anthraquinone with anthracene, $C^{14}H^{10}.C^{14}H^{6}(NO^{2})^{2}O^{2}$, is obtained in violet laminæ belonging to the monoclinic system, by dissolving 9 pts. of the nitro-compound and 10 pts. of anthracene in 100 pts. of coal-naphtha, and leaving the filtered liquid to cool.

On *Disulphanthraquinonic* and *Sulphoxanthraquinonic acids*, see p. 84.

ANTIMONY. Native antimony occurs in veins in Silurian clay-slate in the Russel mine, about 70 miles from Quebec (Weisbach, *Jahrb. Min.* 1867, p. 609).

Respecting the amorphous or explosive antimony deposited from solutions of the metal under certain circumstances by electrolysis (i. 315), the following additional details have been published by Gore (*Chem. Soc. J.* [2] i. 365). This explosive antimony may be obtained from solutions of the bromide or iodide, as well as from the chloride of antimony; but its properties differ to a certain extent according to the nature of the solution used and the mode of deposition.

For the preparation of the explosive antimony it is necessary to use weak currents of constant strength (three elements of Smee's or Grove's battery) and concentrated acid solutions. In electrolysing a solution of antimonious chloride (prepared with 1 pt. antimonious oxide and 5 or 6 pts. hydrochloric acid of sp. gr. 1·12), the current must be of such a strength that the quantity of metal deposited in an hour upon a square inch of the negative electrode (which may consist of copper, silver, or platinum) shall not be less than half a grain; for as soon as this lower limit is reached, the character of the deposit changes suddenly from that of the black amorphous explosive metal to that of pure grey crystalline antimony. In the electrolysis of antimonious bromide (obtained by dissolving 1 pt. antimonious oxide in 10 pts. hydrobromic acid of sp. gr. 1·3) the current must be strong enough to deposit from 3 to 5 grains of antimony per square inch in an hour; for that of antimonious iodide (1 pt. of the oxide dissolved in 15 pts. of aqueous hydriodic acid of sp. gr. 1·25) the current should deposit not more than a grain of antimony per square inch in an hour.

The amorphous antimony deposited from the *chloride* has a density of 5·8. The temperature at which sudden evolution of heat takes place from it varies according to external circumstances: it begins at 77°, but does not attain its full intensity till the entire mass of metal has been heated to 93°–99°; contact with a red-hot wire or scratching with a metallic point sets up the sudden decomposition even at ordinary temperatures. If the metal is surrounded by a good conductor of heat, hot water for example, the evolution of heat takes place gradually.

The metal precipitated from solution of antimonious *bromide* is lighter in colour, duller, and less compact than that obtained from the chloride; its sp. gr. is 5·44. When heated to 121°, and then touched with a red-hot wire, it gives off a considerable quantity of heat with explosive violence; if the metal has not been previously heated to that temperature, the evolution of heat is confined to the part touched by the wire. Scratching the heated substance with a steel point does not give rise to any evolution of heat (when heated to 160°, however, it explodes spontaneously). When fused in a glass tube, it leaves metallic antimony and gives off a volatile substance of buttery consistence, the quantity of which varies in the different layers of one and the same precipitate from 18·4 to 20·5 p. c.: this substance is, according to Gore, a mixture of antimonious bromide with hydrobromic acid.

The third variety of the explosive metal, obtained from the *iodide*, is grey, scaly, of only slightly metallic aspect, and more friable than either of the other two; its sp. gr. is 5·25. It gives out much less heat than the other varieties; the evolution of heat takes place when the metal is heated throughout its mass to 176°; contact with a red-hot wire gives rise to it only when the metal has been previously heated to at least 170°. On the other hand, it is more easily decomposible than the varieties obtained from the bromide and chloride, and often falls to powder even in the electrolytic liquid, giving off hydrogen at the same time. When heated in a tube, it yielded 22·2 p. c. of a solid red fusible sublimate saturated with moisture (antimonious iodide with aqueous hydriodic acid).

All three varieties of amorphous antimony, when moderately and continuously heated to a temperature short of that at which sudden decomposition takes place, give off their heat gradually. They cannot long be preserved without alteration, but after a year or more they exhibit an acid reaction and sourish smell not belonging to them in their original state, and if then digested with dilute hydrochloric and tartaric acid, yield a much larger quantity of soluble substance than they do when recently prepared. Hence Gore regards the explosive metal as a chemical compound—though unstable and in varying proportions—of metallic antimony with a salt of antimony.

Antimonious fluoride when subjected to electrolysis yields nothing but the ordinary crystalline metal.

Reactions of Antimony.—1. The characteristic flame-reactions of antimony are described in the article ANALYSIS (p. 133).

2. *Distinction of Antimony from Tin and Arsenic.*—When a few drops of a solution of antimony acidulated with hydrochloric acid, but free from nitric acid, are placed in contact in a platinum capsule with a piece of metallic zinc, there is formed, immediately in concentrated, more slowly in dilute solutions, a precipitate of metallic antimony, which is brown or black according to the thickness, adheres closely to the platinum, is insoluble in hydrochloric acid either cold or hot, and is easily oxidised by boiling nitric acid. Both the trioxide and the higher oxides of antimony give this reaction, which becomes perceptible, at all events after an half an hour, even in solutions containing only $\frac{1}{30,000}$ pt. of antimony; in still more dilute solutions it becomes doubtful. Tin-solutions (stannous and stannic) yield under the same circumstances an easily loosened deposit of tin, resembling the platinum in colour, and easily soluble in hot hydrochloric acid. The same reaction is exhibited by metastannic acid, when drenched with dilute hydrochloric acid in a platinum capsule, and placed in contact with metallic zinc. Acidulated solutions of arsenious acid treated in like manner with zinc give off arsenetted hydrogen, and yield a deposit of arsenic which partly adheres to the zinc (never to the platinum), partly floats like flocks in the liquid; solutions of arsenic acid behave in a similar manner, but yield a much smaller deposit of arsenic. Tin and arsenic cannot be mistaken for antimony in this reaction; moreover, even when present in considerable quantity, they do not interfere with the characteristic reaction of antimony; indeed when tin is present, the antimony may be distinctly recognised in still more dilute solutions, and identified by its insolubility in hydrochloric acid (Fresenius, *Zeitschr. anal. Chem.* i. 444).

Another method of distinguishing these three metals one from the other, founded on the different behaviour of the sulphides with hydrochloric acid, is given by W. Stein (*Arch. Pharm.* [2] ci. 317). When the mixed sulphides are treated with fuming hydrochloric acid, arsenious sulphide alone remains undissolved. On mixing the acid solution with an equal volume of saturated aqueous hydrogen sulphide, the antimony sulphide is precipitated, and the filtrate, mixed with a larger quantity of the same solution, yields a precipitate of stannic sulphide.

On the different behaviour of arsenetted and antimonetted hydrogen with *iodine*, see ARSENIC.

Quantitative Separation of Antimony from Tin.—Antimonious sulphide, Sb^2S^3, and stannous sulphide, SnS^2, are converted into the corresponding chlorides by dry hydrochloric acid gas, even at ordinary temperatures; the antimonious chloride thus formed volatilises easily in the stream of gas, while the stannous chloride may be heated to incipient fusion without volatilising therein. To render this mode of separation available, however, the tin must be wholly present as stannous salt. If it is in the form of stannic chloride, the separation may be effected by digestion with iron (thin iron plate), in presence of free hydrochloric acid, till the iron is completely dissolved; the antimony is thereby separated in the metallic state, while the tetrachloride of tin is converted into the dichloride. About 3 pts. of iron are required to 1 pt. of antimony (Tookey, *Chem. Soc. J.* xv. 462).

According to Clasen (*J. pr. Chem.* xcii. 477), the separation of tin from antimony by means of iron succeeds particularly well when the quantity of tin is large in proportion to that of the antimony, whereas in the contrary case part of the precipitated antimony redissolves in the acid. In such a case, therefore, it is necessary, before dissolving the alloy [or other mixture or compound of the metals], to add a weighed quantity of tin (from 8 to 10 times the weight of the antimony), which has afterwards to be deducted in estimating the tin. Thin harpsichord wire may be used for the precipitation, and the washing of the antimony (which must be dried at 100° before weighing) is best effected with hot water acidulated at the beginning with a few drops of hydrochloric acid, and finally with absolute alcohol containing a few drops of ether. Moreover, as the pulverised antimony appears not to be quite insoluble in dilute hydrochloric acid, it is best to add iron wire to the solution heated to the boiling point as long as it dissolves. After the precipitation of the antimony, and complete dissolution of the iron, the decanted liquid, acidulated with a little hydrochloric acid, should be further tested with metallic iron, to see if any further separation of antimony will take place (Clasen).

When an alloy of antimony, tin, lead, and a little copper is oxidised with nitric acid, either strong or dilute, the resulting oxides of tin and antimony always retain a little lead, which cannot be washed out, and the quantity of which is greater if the oxidation has been assisted by heat. The complete separation of lead may, however, be easily effected by heating a weighed quantity of the oxides dried at 110° to 120° in a slow stream of dry hydrochloric acid gas, till the tin and antimony are completely volatilised. The solution of the residual lead chloride is added to the nitric acid solution containing the copper and the principal part of the lead, and the tin and antimony in the distilled chlorides are separated by digestion with pure metallic iron, as above described. The antimony after washing with cold water is dried at 110° (Tookey, *loc. cit.*).

Other methods of separating antimony from arsenic, tin, &c., are described in the Dictionary under the several metals.

Volumetric Estimation of Antimony.—Antimonious oxide in alkaline solution reacts with solution of iodine in the same manner as arsenious oxide (i. 265), and may therefore be estimated like the latter. If the antimony is in the form of tartar-emetic, the solution is previously mixed with excess of sodium carbonate, which does not form any precipitate. Free antimonious oxide is dissolved in tartaric acid, and then saturated with sodium carbonate. A commercial sample of tartar-emetic may be valued by comparing it, by means of sodium carbonate and a normal iodine-solution, with a pure sample of the salt.

R. Schneider (*Pogg. Ann.* cx. 634) effects the volumetric estimation of antimony by treating antimonious sulphide with boiling hydrochloric acid, absorbing the evolved hydrogen sulphide in dilute ammonia, and titrating with solution of iodine. One molecule of antimonious sulphide, Sb^2S^3, thus treated gives off $3H^2S$. To perform the estimation, the antimonious sulphide precipitated from a solution containing tartaric acid is well washed on a filter, and decomposed by heating with hydrochloric acid in a small glass flask fitted with a delivery-tube, for conveying the vapours into an inverted retort containing the aqueous ammonia, as in Bunsen's apparatus represented in figs. 48, 49, vol. i. p. 266. This retort is filled with deaërated water containing from 30 to 50 c.c. of strong aqueous ammonia; its contents after cooling are diluted with from half a litre to a litre of deaërated water, according to the quantity of antimonious sulphide used; and a measured volume of this liquid, still in the dilute state, is slightly acidulated with sulphuric acid, and titrated with iodine-solution and starch-solution. Denoting by a the quantity of hydrogen sulphide corresponding to a cub. cent. of iodine-solution, and by t the number of cub. cent. of iodine-solution used, the quantity of antimony is given by the formula:

$$x = \frac{2Sb}{3H^2S} \,.\, a\,t = \frac{2\,.\,122}{3\,.\,34}\,a\,t = 2{\cdot}431\;a\,t.$$

The determination of the hydrogen sulphide may be made more exact by receiving the gas evolved in the same apparatus in a neutral or slightly alkaline solution of sodium arsenite, and titrating the remaining portion of arsenious acid with solution of iodine. The solution of the sodium arsenite contains in the cubic centimetre about 0·005 or 0·006 grm. of arsenious acid, and is most easily compared with an iodine-solution of known strength, by adding to a known quantity of the arsenic solution, first a few drops of hydrochloric acid sufficient to produce an acid reaction, then an excess of sodium bicarbonate, a small quantity of starch-solution, and finally the iodine-solution. The hydrochloric acid gas which passes over into the receiver together with the hydrogen sulphide soon renders the liquid acid, and throws down arsenious sulphide. The contents of the retort when cold are mixed with a little tartaric acid and diluted to a known volume, and in a measured portion of the filtered liquid, after supersaturation with sodium bicarbonate, the amount of arsenious acid is determined by solution of iodine. Denoting the volume of iodine-solution corresponding to the arsenic-solution used by V, that of the iodine-solution corresponding to the arsenic-solution after the distillation has been performed, by v, and the quantity of iodine in a cub. cent. of the iodine-solution by a, the quantity of antimony sought is:

$$x = \frac{Sb}{I}\,(V - v)\,a = 0{\cdot}96\,(V - v)\,a.$$

Guyard (*Bull. Soc. Chim.* 1863, p. 89) gives the following method, founded on the fact that antimonious oxide in dilute very acid solution, when freed from all foreign metals, is converted by potassium permanganate into antimonic acid. A solution of 1 to 1½ grm. of the antimony-compound to be tested is supersaturated with ammonia and yellow ammonium sulphide, and the antimonious sulphide separated from the filtrate by dilute hydrochloric acid is dissolved in strong hydrochloric acid. The solution mixed with a little tartaric acid is filtered, freed from hydrogen sulphide, diluted to about a litre, and then titrated with a solution of potassium permanganate till a red coloration is produced. The value of this solution must be previously fixed by titration with antimonious sulphide, or, better, with tartar-emetic, so that 30 c.c. may correspond to 1 grm. of antimony.

ANTIMONY BROMIDE. $SbBr^3$.—Nicklès (*Compt. rend.* xlviii. 837) prepares this compound by treating pulverised antimony with bromine dissolved in carbon bisulphide. The bromide dissolves in the liquid, and crystallises therefrom in rhombic pyramids, often assuming the form of flattened prisms from development of the end-faces (according to Nicklès, prisms of 69°, with acuminations of 80°; angle of the contiguous pyramidal faces = 181°).

ANTIMONY CHLORIDES. When a solution of antimonious oxide or antimonious sulphide is distilled with hydrochloric acid, a portion of that acid passes over first, together with the aqueous vapour, and then *antimonious chloride*, which ultimately passes over quite anhydrous. In the distillation of a hydrochloric acid solution of antimony containing nitric acid, this acid and hydrochloric acid are volatilised, but no antimony, till finally, after all the nitric acid has escaped, a small quantity of antimony pentachloride is volatilised (H. Rose, *J. pr. Chem.* lxxvi. 137).

Antimonious chloride unites with *aniline hydrochloride*, forming the crystalline compound $3C^6H^7N.SbCl^3$, or $[(C^6H^5)^3Sb'''H^6]'''N^3.Cl^3$ (Schiff; see PHENYL-AMMONIUMS, iv. 474).

When 1 mol. antimonious chloride and 3 mol. alcohol are heated to 150° in a sealed tube, ethyl chloride and hydrogen chloride are formed, together with crystals of an oxychloride, $Sb^4O^5Cl^2 = 2SbOCl.Sb^2O^3$ (algaroth powder). These crystals are monoclinic but nearly right-angled rhombic prisms, having their acute edges bevelled. When 1 mol. antimonious chloride is heated with 1 mol. alcohol to 160° for several hours, ethyl chloride and hydrogen chloride are also formed, together with crystals of antimonious oxychloride, SbOCl. These crystals are soluble in alcohol and ether, and are partly decomposed by water into hydrochloric acid and algaroth powder, $Sb^4O^5Cl^2$ (Schäffer, *Zeitschr. f. Chem.* [2] iv. 506; further, *Ann. Ch. Pharm.* clii. 314).

A compound of *antimonic chloride* with *nitrous oxychloride*, $SbCl^5.NOCl$, is obtained by passing the vapour of nitrogen tetroxide into antimonic chloride. It forms a dry sulphur-yellow, very hygroscopic powder, which, when heated, volatilises without previous fusion, leaving a small quantity of antimonic oxide. The distillate solidifies in the crystalline form after complete cooling. It is decomposed by water, but dissolves without turbidity in aqueous tartaric acid (R. Weber, *Pogg. Ann.* cxxiii. 347).

Antimonic chloride likewise forms definite compounds with the higher *chlorides of phosphorus, selenium*, and *sulphur*. The compound $SbCl^5.PCl^5$ is produced by heating antimonious or antimonic chloride with phosphorus pentachloride, and remains, after distilling off the excess of the more volatile chlorides, as a slightly volatile, infusible, spongy yellow mass, which quickly absorbs water from the air. The compound with *phosphoric oxychloride*, $SbCl^5.PCl^3O$, separates on mixing antimonic chloride with an excess of phosphoric oxychloride, as a white, deliquescent, crystalline substance, which must be dried on a brick over sulphuric acid and lime. The *selenium compound*, $SbCl^5.SeCl^4$, is prepared by treating a mixture of 1 at. selenium and 1 at. antimony fused and cooled again, with chlorine, out of contact with air, and freeing the resulting whitish mass from excess of antimonic chloride by draining on a brick. Antimonious selenide treated with chlorine forms a pulverulent mass, which appears to be a mixture of the preceding compound with selenium chloride. The sulphur compound, $SbCl^5.SCl^4$, is formed, together with free sulphur, by the action of dry chlorine on antimonious sulphide, and remains, on warming the product, as a dry powder which dissolves in dilute nitric acid, without separation of sulphur (R. Weber, *Pogg. Ann.* cxxv. 78). H. Rose assigns to this last compound the formula $2SbCl^5.3SCl^4$ (v. 536).

A *hydrate of antimonic chloride*, $SbCl^5.4H^2O$, separates, when a solution of the chloride in the smallest possible quantity of water is left to stand over oil of vitriol, in deliquescent crystals, which may be recrystallised without decomposition from a small quantity of water. The trichloride does not form a hydrate under similar circumstances. A small quantity of water mixes with it, without turbidity, and a mixture of it with a somewhat larger quantity of water left to evaporate over oil of vitriol ultimately yields anhydrous crystals of antimonious chloride.

ANTIMONY FLUORIDES. *Antimonious fluoride*, SbF^3, is obtained by dissolving antimonious oxide in hydrofluoric acid. The solution slowly evaporated between 70° and 90° deposits the compound in rhombic octohedrons; by more rapid evaporation it is obtained in prisms, and by still more rapid evaporation in presence of an excess of acid, in small scales. Antimonious fluoride is deliquescent, and has a sharply acid taste, with styptic after-taste; dissolves easily in water, forming a solution which does not become turbid on dilution. The solution, if evaporated without addition of acid, deposits at a certain degree of concentration an insoluble powder, probably an oxyfluoride, which immediately redissolves on addition of hydrofluoric or hydrochloric acid; the same compound separates when the crystals deliquesce in the air, and when thus formed exhibits nearly the composition $2SbF^3 . Sb^2O^3$ or $Sb^4F^6O^3$; it appears also to be produced by the action of hydrofluoric acid on an excess of antimonious oxide. Antimonious fluoride heated in a retort containing air yields a sublimate consisting of hard, very deliquescent crusts interpersed with slender needles, and leaves a copious residue of antimonious oxide (Flückiger, *Ann. Ch. Pharm.* lxxxiv. 248).

Antimonious fluoride unites with the fluorides of the alkali-metals, forming double salts containing 1, 2, and 3 mols. of alkaline fluoride to 1 mol. of antimonious fluoride; but the last-mentioned proportion is known only in the case of the sodium salt. These double fluorides decompose when heated in contact with the air, with formation of antimonious oxide. When wrapped up in a thin plate of sodium, and sharply struck, they decompose suddenly, with detonation and deflagration. The *ammonium-salt* $2NH^4F . SbF^3$ is obtained by dissolving antimonious oxide and ammonium carbonate in excess of hydrofluoric acid and evaporating. It crystallises in anhydrous rhombic tables ($oP . \infty P . P$) and prisms ($\infty P . \breve{P}\infty . \infty\breve{P}\infty$, with the angle $\infty P : P =$ about 88°). It absorbs water from moist air, and dissolves in 0·9 pt. water at ordinary temperatures, with production of cold. The solution is acid, attacks glass strongly, and is precipitated by alcohol and ether. The dry salt is infusible, does not give off ammonia at 140°, volatilises completely when quickly heated in an open platinum crucible, but is partly decomposed by slow heating, giving off ammonium fluoride, and leaving antimonious oxide. The *lithium salt* $2LiF . SbF^3$ crystallises with difficulty in large ill-defined prisms requiring more than 20 pts. of water for solution. The *dipotassic salt* $2KF . SbF^3$ is formed by dissolving 1 mol. of antimonious oxide and about 3 mol. of potassium carbonate in excess of hydrofluoric acid, and separates from the concentrated solution in small laminæ, or by slow cooling, and especially when a saturated solution is evaporated at 60°–70°, in large thin transparent rectangular laminæ or tables. Sometimes also acute octohedrons or rhombic laminæ are formed, which become opaque if left in the liquid for some days, but by solution or evaporation are converted into the ordinary crystals. Potassio-antimonious fluoride is acid, has a sour taste with astringent after-taste, dissolves in 9 pts. of water at 13°, and in less than 2 pts. at the boiling heat; insoluble in alcohol and ether. The dry salt does not lose weight at 120°; it melts at a red heat, and solidifies on cooling to a radio-crystalline mass. It etches glass in the moist, but not in the dry state. The *monopotassic salt* $KF . SbF^3$ is formed by dissolving 1 mol. of antimonious oxide and 1 mol. of potassium carbonate in hydrofluoric acid; the solution saturated while warm yields large hard rhombic crystals, which become turbid on exposure to the air, or by slower cooling in soft slender silky needles; it dissolves in 2⅔ pts. water. The *sodium salt* $3NaF . SbF^3$ is formed by mixing a solution of 1 mol. of antimonious oxide ($Sb\,O^3$) in excess of hydrofluoric acid, with 6 mol. of sodium fluoride (NaF), and separates on cooling in small shining transparent prisms. It melts when strongly heated, dissolves in 14 pts. of water at ordinary temperatures, and in 4 pts. at the boiling heat, forming an acid solution (Flückiger, *loc cit.*).

Antimonic Fluoride. SbF^5 (Marignac, *Ann. Ch. Pharm.* cxlv. 237).—This compound is easily formed by dissolving antimonic hydrate in hydrofluoric acid, and remains on evaporation in a vacuum as a gummy mass; the solution, when evaporated by heat, leaves a white insoluble residue, apparently an oxyfluoride. By adding potash, soda, or ammonia to the solution acidulated with hydrofluoric acid, double fluorides are produced, which are very soluble, and crystallise with difficulty; they are permanent in the air in the solid state, but alterable in solution, and are partly converted by repeated evaporation into oxyfluorides. Their aqueous solutions are not precipitated by acids, alkalis, or hydrogen sulphide. They are not isomorphous with the corresponding double fluorides of tantalum and niobium.

Ammonio-antimonic fluoride, $NH^4F . SbF^5$, forms needle-shaped hexagonal prisms acuminated with a rhombohedron, whose terminal edges form an angle of about 96°. The solution mixed with excess of ammonium fluoride and left to evaporate deposits the *diammonic salt* $2(2NH^4F . SbF^5) . H^2O$ in rectangular flattened prisms, exhibiting the combination $\infty P . \infty\breve{P}\infty . oP$, with P and several undeterminable faces subordinate. Angle $\infty P : \infty P = 9\ {}^\circ\ \ \infty\breve{P} : \infty\breve{P}\infty = 134° 25'$; $\infty P : P = 148° 25'$.

The *monopotassic salt* $KF . SbF^5$ crystallises in thin tablets from a solution of gummy potassium antimonate in aqueous hydrofluoric concentrated by evaporation. The solution mixed with excess of potassium fluoride and evaporated, yields the *dipotassic salt* $2KF . SbF^3 . 2H^2O$ in beautiful shining monoclinic prisms exhibiting the combination $\infty P . \infty P\infty . [P\infty] . +P . -P . +2P\infty . -2P\infty$, the hemi-pyramids however occurring but rarely and subordinately. Angle $\infty P : \infty P = 58°$; $\infty P : \infty P\infty = 119°$; $\infty P\infty : [P\infty] = 91°$; $[P\infty] : [P\infty]$ over the principal axis $= 83° 16 : -P : -P = 92° 50'$; acute angle of the axes $= 89° 16'$. The salt melts at about 90° in its water of crystallisation, and dries up, with evolution of hydrofluoric acid, to a gummy mass no longer soluble in water.

Sodio-antimonic oxyfluoride, $NaF.SbOF^3.H^2O$, is obtained by adding sodium carbonate to a solution of antimonic fluoride containing free hydrofluoric acid, and crystallises by spontaneous evaporation in small deliquescent hexagonal prisms with rhombohedral or six-sided pyramidal summits. By adding hydrofluoric acid to a solution of this salt, and leaving the liquid to evaporate, *sodio-antimonic fluoride*, $NaF.SbF^5$, is obtained in cube-like forms, which however are double-refracting. It decomposes readily in solution, and on evaporation the oxyfluoride is again obtained.

ANTIMONY HYDRIDE. SbH^3. *Stibine. Antimonetted Hydrogen.*—This gas has not yet been obtained pure, but only mixed with hydrogen. According to Th. Humpert (*Chem. Centr.* 1865, p. 86), a gas containing a rather large proportion of stibine is obtained by decomposing a concentrated solution of antimonious chloride with sodium amalgam, part of the stibine thus evolved being however immediately decomposed and coating the sides of the flask with a thick layer of antimony. Rieckher (*Jahresb.* 1867, p. 255) finds that when antimonious solutions are decomposed by zinc and dilute acid, the quantity of antimony precipitated as metal is to that evolved as stibine, in proportions varying from 95 : 8 to 96 : 4, so that only a small fraction passes off as stibine.

Stibine is decomposed by strong sulphuric acid (but more slowly than arsine, with evolution of hydrogen sulphide, and separation of a velvet-black powder containing antimony and hydrogen; also antimonious sulphide, if the passage of the gas into the acid be continued for a long time (Humpert, *loc. cit.*). According to Dragendorff (*Zeitschr. anal. Chem.* v. 200), stibine, whether dry or moist, is decomposed by solid potassium hydrate, which thereby becomes covered with a metallically lustrous film, probably consisting of potassium antimonide, which quickly disappears in contact with water or moist air. Arsine, on the contrary, is not decomposed by potash. On passing a mixture of the two gases through a tube three or four inches long, containing lumps of potassium hydrate about as large as peas, the stibine is completely absorbed. while the arsine passes on unaltered. Drying tubes containing potash must therefore be avoided in the preparation of stibine, whereas the detection of arsenic as arsine in presence of antimony is simplified by their use. Potash-ley of sp. gr. 1·25 acts upon stibine in the same manner as the solid hydrate, though not so quickly.

Respecting the action of iodine on stibine, and the method founded thereon of distinguishing antimony from arsenic, see ARSENIC.

ANTIMONY IODIDES. Nicklès obtains *antimonious iodide*, SbI^3, in the same manner as the bromide (p. 184). It forms red tabular crystals, permanent in the air, and consisting of the hexagonal combination $oP . P .$ &c.; basal angle of the double pyramid, 133°; terminal, 120°. Schneider (*Pogg. Ann.* cix. 609) obtains this compound in crystals of considerable size by heating a mixture of 1 mol. antimonious sulphide and 6 at. iodine. An orange-red sulphiodide then sublimes at first, and condenses on the upper part of the flask in small laminæ and needles, while the tri-iodide SbI^3 condenses on the lower and hotter parts of the flask in large, thin, poppy-red, hexagonal plates similar to those obtained by Nicklès; the compound is isomorphous with the tri-iodides of arsenic and bismuth. It dissolves slowly but completely in carbon bisulphide, and separates on cooling in small, sharply defined, shining laminæ, of somewhat lighter colour than that obtained by sublimation. It is quickly decomposed by alkaline hydrates and carbonates, yielding pure antimonious oxide (Schneider).

Antimonious iodide forms double salts with the iodides of the more positive metals. They are prepared by adding pulverised antimonious iodide to warm saturated solutions of the several iodides, and evaporating the filtered solutions at mean temperatures. The *potassium salt* $3KI.2SbI^3.3H^2O$ forms dark black-brown rectangular laminæ, ruby-red by transmitted light, becoming anhydrous at 100°, and then assuming a cinnabar-red colour. The *sodium salt* $3NaI.2SbI^3.12H^2O$ forms light orange-red rectangular prisms acuminated by four faces resting on the prismatic edges; it becomes anhydrous and orange-coloured at 100°. There are three *ammonium salts*. A warm saturated solution of 1 mol. of antimonious iodide in 3 mols. of ammonium iodide first deposits the salt $3NH^4I.4SbI^3.9H^2O$ in scarlet rectangular prisms, becoming crimson when anhydrous; then successively the following salts: $3NH^4I.2SbI^3.3H^2O$ in dark black-brown rectangular laminæ, ruby-red by transmitted light, resembling the potassium salt, becoming carmine-red when anhydrous; and $4NH^4I.SbI.3H^2O$, in large almost black rectangular prisms, acuminated with four faces resting on the prismatic edges, translucent with ruby-red colour in thin layers, carmine-red when anhydrous. The *barium salt* $BaI^2.SbI^3.9H^2O$ forms translucent rhombic prisms of 105° 32′ with perpendicular end-faces, having a vitreous lustre, and translucent, with deep orange-red colour. All these salts are decomposed by water, with separation of antimonious oxy-iodide; they dissolve in hydrochloric and in acetic acids with yellow colour, in tartaric acid without colour, give up antimonious iodide to carbon bisulphide, and are decomposed by strong sulphuric acid, with separation of iodine and evolution of hydriodic acid. The compounds containing fixed metallic iodides are decomposed when heated in a tube, yielding a sublimate of antimonious iodide and a residue of the fixed iodide; the ammonium salts sublime completely, with partial decomposition and separation of iodine-vapours (J. Schäffer, *Pogg. Ann.* cix. 611).

Nicklès (*Compt. rend.* li. 1097; *Jahresb.* 1860, p. 176) has described several groups of double salts of antimonious iodide, which he finds to be isomorphous with the corresponding bismuth-compounds. Among these he especially particularises two groups, viz. $mI.MI^3.2H^2O$ and $mI.MI^3.H^2O$; also the corresponding bromides $mBr.MBr^3.H^2O$ [where m = K, Na, or NH^4, and M = Sb or Bi]. The compounds containing $2H^2O$ crystallise in right rhombic prisms of 97°; those with H^2O in right rhombic prisms of 136° 35′, with a dome and many secondary faces. The compounds prepared by Nicklès, some of which contain bismuth and antimony replacing one another isomorphously, are:

α. $NH^4I.SbI^3.2H^2O$
β. $NH^4I.(Bi,Sb)I^3.2H^2O$
γ. $NH^4I.BiI^3.H^2O$
δ. $NaI.BiI^3.H^2O$
ε. $KI.BiI^3.H^2O$
ζ. $NH^4Br.BiBr^3.H^2O$
η. $NH^4Br.Bi(Br,I)^3.H^2O$
θ. $KI.SbI^3.H^2O$
ι. $NaI.(Bi,Sb)I^3.H^2O$

The compounds α, γ, δ, and ι were obtained by the action of iodine or bromine on antimony or bismuth, in presence of a saturated solution of ammonium, potassium, or sodium chloride; a double iodide or bromide then crystallises out, while a double chloride remains in solution. β crystallises from the mixed alcoholic solution of potassio-antimonious iodide and ammonio-bismuthous bromide. θ crystallises, together with other compounds, from a solution of antimony in alcohol containing iodide or chloride of potassium; ζ from a solution of bismuth in alcohol or ether containing bromine and a little ammonium bromide. The crystals of α are red, of β black (red when pulverised); ζ forms yellow needles. These double salts are decomposed by water, and even by unsaturated solutions of alkaline chlorides, bromides, or iodides. Most of them are rendered turbid by alcohol, but ζ is soluble in that liquid. They give up the whole of their water over oil of vitriol, as well as when heated to 100°; some, especially α and ζ, appear to undergo decomposition at that temperature. In violet light these double salts acquire a reddish colour, especially the bismuth-compounds, which are for the most part yellow, brown, or black; the black iodide of bismuth likewise turns red in violet light (Nicklès).

The isomorphism of corresponding bismuth and antimony compounds is also confirmed by Linau's investigations of certain double salts of bismuth iodide, which appear to have the same crystalline form as the analogous antimony-compounds examined by Schäffer. See BISMUTH.

Antimonic Iodide, SbI^5, is formed, according to Van der Espt (*Arch. Pharm.* [2] cxvii. 115), by heating 1 pt. of antimony with 5 pts. of iodine; it then sublimes in red transparent laminæ, decomposible by water into hydriodic and antimonic acids. It is also said to be produced by passing antimonetted hydrogen into an alcoholic solution of iodine. But, as the crystals obtained by these processes have the same form as those of the triodide (p. 186), these statements must be regarded as somewhat doubtful.

ANTIMONY OXIDES. *Antimonious oxide*, Sb^2O^3, occurs in Borneo in the form of a yellowish or reddish-white compact mass, having a crystalline structure, and yielding a yellowish-white powder. Here and there it occurs in rhombic prismatic crystals, half an inch long, with dihedral summits, horizontally striated, and having a nacreous lustre. Sp. gr. 4·64 to 4·68. It appears to have been formed by oxidation of the trisulphide (antimony-glance), which is found imbedded in it (Phipson, *Compt. rend.* lii. 752). Hallett and Stenhouse have proposed the use of antimony tetroxide, Sb^2O^4, prepared by roasting this native oxide, as a white pigment. It has the advantage of not being blackened by hydrogen sulphide, but is inferior to zinc-white, barium sulphate, and white lead in whiteness and opacity (*Repertory of Patent Inventions*, 1861, Nov. p. 374; *Dingl. pol. J.* cxlii. 373; *Hofmann's Report*, 1862, p. 79).

W. Lindner (*Zeitschr. f. Chem.* [2] v. 442) prepares antimonious oxide by dissolving the native sulphide in a rather strong solution of ferric chloride containing a slight excess of hydrochloric acid. The antimony then dissolves in a very short time, without evolution of noxious gases, and the whole of the sulphur is precipitated. By diluting with water, and washing the resulting precipitate, a very pure algaroth powder is obtained, which when treated with soda yields pure antimonious oxide.

Antimonious oxide is obtained in the prismatic form by the action of water at 150° on the oxychloride (Debray, *Compt. rend.* lviii. 1209). According to Terreil (*ibid.* lxii. 302), the prismatic oxide is always produced in the combustion of the metal and in the roasting of antimonious sulphide; the octohedral form, on the other hand, when the prismatic oxide is sublimed at a dull red heat in non-oxidising gases; by rapid sublimation the octohedral crystals are reconverted into the prismatic. The two forms may be produced simultaneously by passing a slow stream of dry air through a porcelain tube containing a boat filled with metallic antimony, the tube being at first heated only where the metal is placed, but after a few hours likewise at the point where the prismatic oxide might condense. After the operation has been continued for 12 hours, prisms alone are found in the neighbourhood of the metal, prisms with implanted octohedrons at some distance further, and pure octohedrons at the end of the tube. These artificial oxides agree perfectly in their properties with the native varieties of the oxide (i. 323). The sp. gr. of the artificial prismatic oxide is 3·72, that of the native 3·70. The prismatic oxide is more easily attacked by reagents, and especially more readily dissolved by acids and alkalis than the octohedral oxide; ammonium sulphide colours it brown-red and finally dissolves it. The artificially prepared octohedral oxide has a sp. gr. of 5·11 (that of Senarmontite is 5·20); in the crystallised state it resists the action of ammonium sulphide, but is attacked by it when pulverised. The octohedral oxide, said to be obtained by crystallisation from alkaline solutions (i. 323), consists, according to Terreil, of hydrated sodium antimonite.

Antimonites.—A solution of antimonious oxide in caustic soda yields crystals of sodium antimonite containing 1 or 3 at. antimony to 1 at. sodium, according to the degree of concentration. The *mono-antimonite* $NaSbO^2.3H^2O$ or $Na^2O.Sb^2O^3.6H^2O$, which is the salt most frequently obtained, crystallises in octohedrons, apparently trimetric; they are colourless, have a strong lustre and a sp. gr. of 2·864. When heated they give off their water and become opaque. They dissolve with difficulty in boiling water, and separate almost completely as the solution cools. The solution, which is usually opalescent, has an alkaline reaction and is not precipitated by acids, alkalis, or alkaline earths; by barium chloride, only after addition of ammonia. With plumbic, cupric, mercurous, and ferric salts, it forms precipitates soluble in nitric acid; with argentic nitrate, a white precipitate which is soluble in dilute nitric acid, and is first turned brown by ammonia, then decolorised and dissolved. Hydrogen sulphide colours the aqueous solution yellow. The *triantimonite* $NaSbO^2.Sb^2O^3.H^2O$ or $Na^2O.3Sb^2O^3.2H^2O$ forms less easily than the mono-antimonite, and is obtained only from very concentrated alkaline solutions, in rather large crystals, also belonging to the trimetric system, and having a sp. gr. of 5·05. They are nearly insoluble in water. By ammonium sulphide, they are first coloured brown-red and then dissolved, a character which distinguishes them from the octohedral oxide. *Potassium antimonite* has not been obtained in crystals. Those which frequently separate from a solution of antimonious oxide in potash-ley consist of the sodium salt, and arise from the presence of soda in the potash-ley; they are also gradually formed on adding a sodium salt to a solution of pure potassium antimonite (Terreil).

Antimonic Oxide and ***Acid.***—Antimonic oxide or acid is reduced by stannous chloride in acid solution to antimonious oxide (Streng, *Pogg. Ann.* xciv. 493); and this, according to Kessler (*Jahresb.* 1861, p. 265), is not further altered, even by boiling in a concentrated acid solution with excess of stannous chloride. According to Schiff (*Ann. Ch. Pharm.* cxx. 47; *Jahresb.* 1861, p. 277), antimonic acid treated with stannous chloride at ordinary temperatures is converted into a yellow substance, which, if the action be allowed to continue at 80°, becomes deeper in colour, and after about an hour's heating changes into red hydrated stannous antimonate, $SnSb^2O^6.2H^2O$ or $SnO.Sb^2O^5.2H^2O$, which becomes yellowish-grey when deprived of its water. There appears also to be a stannous di-antimonate, $SnO.2Sb^2O^5$. When anhydrous antimonic oxide is heated for 8 or 10 hours with stannous chloride to

35°–40° a yellow substance is obtained, agreeing approximately with the formula $2SnO.3Sb^2O^5.4H^2O$; anhydrous antimonic oxide did not yield a brick-red tin salt.

Potassium antimonate heated in vapour of carbon bisulphide yields a dark-brown product, probably consisting of potassium sulphantimonite, $KSbS^2$, formed according to the equation:

$$4KSbO^3 + 5CS^2 = 4KSbS^2 + 3CO^2 + 2CO + 2SO^2.$$

Ammonium antimonate is converted by heating with carbon bisulphide into a volatile ammonium polysulphide and fused antimonious sulphide (W. Müller, *Pogg. Ann.* cxxvii. 404).

ANTOZONE. See Ozone (iv. 302).

ANTOZONITE. A name applied by Schönbein to a variety of fluor-spar, found at Wölsendorf in the Bavarian Oberpfalz, and at Joachimsthal in Bohemia, in which Schrötter had demonstrated the presence of a small quantity of ozone, the mineral emitting the odour of ozone when heated, and liberating iodine from potassium iodide, and chlorine from sodium chloride. Schönbein supposed that it contained the electro-positive variety of oxygen, which he designated as antozone (*Jahresb.* 1860, p. 58; 1861, p. 1034; 1863, p. 842).

APPLE. See Fruit (ii. 710).

APPLE-TREE BARK. The aqueous decoction of the root-bark of this tree yields with neutral lead-acetate a precipitate, the greater part of which dissolves in acetic acid. On decomposing the *insoluble* portion with hydrogen sulphide and evaporating the filtrate, a syrupy residue is obtained, which when treated with alcohol is resolved into insoluble pectin and a small quantity of a substance which crystallises from the alcoholic solution on evaporation in a vacuum. This last substance gives off 6·74 p. c. water at 100°, and its composition then agrees with the formula $C^{24}H^{30}O^{27} = C^6H^6O^6 + 3C^6H^8O^7$. The acetic acid solution of the lead precipitate yields with basic lead acetate a small additional quantity of the lead-compound of this body. The liquid filtered therefrom yields on addition of ammonia a copious precipitate; and by decomposing this precipitate in like manner with hydrogen sulphide and evaporating the filtrate, crystals of calcium-phloretin are first obtained, from which the phloretin (iv. 492) may be separated by hydrochloric acid. The mother-liquor separated from the calcium-compound yields with ammonium sulphide a precipitate from which (by solution in water containing acetic acid, precipitation with lead acetate, and decomposition of the washed precipitate with hydrogen sulphide) a tannin is obtained identical with that which is contained in horse-chestnut bark. The stem-bark of the apple-tree contains a yellow colouring matter (Rochleder, *J. pr. Chem.* xcviii. 205; *Jahresb.* 1866, p. 694).

APHRODÆSCIN. A substance contained, according to Rochleder, in the cotyledons of the horse-chestnut (iii. 172).

APIUM. When an aqueous extract of celery-root (*Apium graveolens*) is subjected to dialysis, a solution of pure mannite first passes through the parchment-paper, then a solution of extractive matter and potassium salts of vegetable acids, whilst a liquid remains behind, containing a substance intermediate in its properties between gum and pectin, and gelatinising when mixed with alcohol (H. Reinsch, *Jahresb.* 1863, p. 612).

APLYSIA. The colouring matter secreted by a vesicular organ of the sea-owl or lump-fish (*Aplysia depilans*), a gasteropod occurring on the coasts of the Mediterranean and of Portugal, is, according to Ziegler (*J. pr. Chem.* ciii. 63), a concentrated solution of aniline red and aniline violet. In the dissolved state this offensive-smelling colouring matter decomposes very readily. On precipitating it by sulphuric acid, and then again from alcoholic solution by common salt, a substance is obtained which exhibits all the reactions of aniline violet. The red colouring matter, which remains in solution after the precipitation by common salt, and may be separated by tannic acid, is, like fuchsine, decolorised by ammonia and turned red again by acetic acid.

APOCODEINE. See Codeine.

APOMORPHINE. See Morphine.

APOSORBIC ACID. $C^5H^6O^7$.—An acid produced, together with several modifications of tartaric acid, by the action of nitric acid upon sorbin. The acid syrup remaining after the dextro- and lævo-tartaric acids have been separated as completely as possible as acid ammonium salts, contains aposorbic and mesotartaric acids (v. 688), which may be separated, though not very completely, with calcium acetate and lead acetate. The aposorbic acid, which is contained chiefly in the lead precipitate, crystallises in confused laminæ, more rarely in thin acute rhombohedrons. It dissolves in 1·63 pts. water at 15°; does not lose weight at 100°; melts at about 110° with loss of water; boils and becomes coloured at 170°; and decomposes at 200°, leaving a black blistered mass, and yielding a distillate which does not contain pyroracemic acid.

Silver aposorbate, $C^5H^6Ag^2O^7$, does not crystallise. The *calcium salt* contains $C^5H^6Ca''O^7.4H^2O$, the *lead salt* $C^5H^6Pb''O^7.PbO$. The *ammonium salt*, which crystallises in silky needles, is easily soluble, and is not precipitated either by potassium acetate or by mercuric nitrate; the calcium salt however, like the tartrate, is soluble in sal-ammoniac and in potash (Dessaignes, *Rép. Chim. pure*, v. 41; *Ann. Ch. Pharm. Suppl.* ii. 242).

AQUACREPTITE. A magnesio-ferric silicate from Chester Co., Pennsylvania, so called from its property of disintegrating with decrepitation when thrown into water. It occurs in a narrow band of serpentine. It is compact, opaque, fragile, with slightly conchoïdal fracture; adheres to the tongue; has a yellowish-brown colour, and yields an orange-yellow powder. Hardness = 2·5. Sp. gr. = 2·05 – 2·08. After calcination it dissolves in nitromuriatic acid, the silica however separating in flocks; gives by analysis 41·00 – 43·03, SiO^2, 17·60 – 19·58 MgO, 12·30 – 13·30 ferric oxide, 4·00 – 6·71 alumina, and 16 to 23 water (C.U. Shepard, *Sill. Am. J.* Sept. 1858, p. 256; *Bull. Soc. Chim.* [2] xi. 242).

ARACHIDIC ACID, $C^{20}H^{40}O^2$ (melting at 75°), is obtained nearly pure, together with a very small quantity of oleic acid, by saponifying the fat obtained from the kernels of the fruits of *Nephelium lappaceum*, an East Indian plant. This fat melts at 65°, and after recrystallisation at 68·5° (Oudemans, *J. pr. Chem.* xcix. 407; *Jahresb.* 1866, p. 696).

ARAUCARIA. In the juice of *Araucaria brasiliana*, which solidifies to a resin, Peckolt (*Chem. Centr.* 1865, p. 1070) found—besides gum, sugar, vegetable mucilage, and extractive-matter—a volatile oil smelling like oil of juniper, and several resins partly soluble in cold, partly in boiling alcohol.

ARBUTIN. $C^{12}H^{16}O^7$.—This substance, discovered by Kawalier in the leaves of the red bearberry, *Arctostophylos Uva Ursi* (i. 354), has been further examined by Strecker (*Ann. Ch. Pharm.* cvii. 229), and by Zwenger and Himmelmann (*ibid.* cxxix. 203), who have likewise obtained it from the leaves of a species of winter-green, *Pyrola umbellata*. It is prepared by precipitating the aqueous decoction of the leaves of either of these plants with basic lead-acetate, filtering, removing the excess of lead with hydrogen sulphide, and either treating the filtrate with animal charcoal and leaving it to crystallise (Strecker), or evaporating and digesting the residue with a mixture of 8 pts. ether and 1 pt. alcohol, which dissolves out the arbutin, and deposits it on evaporation in the crystalline state (Zwenger a. Himmelmann).

Arbutin crystallises in tufts of colourless silky needles, having a bitter taste, easily soluble in alcohol and in boiling water, very sparingly soluble in ether, melting at 170°. When dried at 100° it exhibits the following composition:—

Calculation.			Analyses.				
			Kawalier.		Strecker.		Zwenger a. Himmelmann.
C^{12}	144	52·6	52·4	52·6	52·5	53·1	52·5
H^{16}	16	5·9	6·2	6·1	5·9	5·9	6·3
O^7	112	41·5					
	272	100·0					

Kawalier represented it by the formula $C^{32}H^{44}O^{19}$, requiring 52·5 C and 6·0 H; but this formula, though it agrees closely with his analyses, does not explain the transformations of arbutin so well as the formula $C^{12}H^{16}O^7$ proposed by Strecker.

Crystallised arbutin (air-dried) contains 51·0 p. c. carbon and 6·3 hydrogen, agreeing nearly with the formula $2C^{12}H^{16}O^7.H^2O$ (Strecker); the water of crystallisation (3·2 p. c.) goes off at 100°.*

The solution of arbutin is not precipitated by plumbic or ferric salts, and does not reduce an alkaline solution of cupric oxide. When boiled with dilute sulphuric acid, or subjected in aqueous solution to the action of emulsin, or of an analogous ferment contained in the bearberry, it is resolved into glucose and hydroquinone (Kawalier's arcturin):

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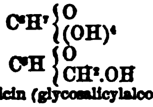
* Zwenger a. Himmelmann obtained, with arbutin prepared from winter-green (but not with that prepared from bearberry), crystals containing 2 at. or 11·7 p. c. water.

$$C^{12}H^{16}O^7 + H^2O = C^6H^{12}O^6 + C^6H^6O^2 \text{ (Strecker).}$$

Hydroquinone—but not its isomeride, pyrocatechin—is also found among the products of the dry distillation of arbutin (Zwenger a. Himmelmann).

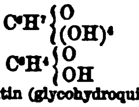
The resolution of arbutin into glucose and hydroquinone is analogous to that of salicin, $C^{13}H^{18}O^7$, into glucose and saligenin, $C^7H^8O^2$. Salicin in fact differs from arbutin, and saligenin from hydroquinone by CH^2 (Strecker).

Arbutin oxidised with manganese dioxide and sulphuric acid, yields quinone, $C^6H^4O^2$, and formic acid. On passing chlorine through its aqueous solution, the liquid turns yellow or red, and after a while deposits yellow shining laminæ of chlorinated quinone—probably a mixture of $C^6H^2Cl^2O^2$ and $C^6H^3ClO^2$. It dissolves in strong nitric acid, and on adding alcohol to the liquid, yellow needles are deposited, which when purified by recrystallisation exhibit the composition of dinitro-arbutin, $C^{12}H^{14}(NO^2)^2O^7$. This substance is very soluble in water, less soluble in alcohol, insoluble in ether. It melts when heated and recrystallises on cooling. Its solutions are not precipitated by metallic salts. By boiling with acids, it is resolved into glucose, and an easily soluble crystallisable substance, probably consisting of dinitrohydroquinone, $C^6H^4(NO^2)^2O^2$ (Strecker). The relations between salicin and arbutin may be represented by the following formulæ:



$$\begin{array}{l} C^6H^7\left\{\begin{array}{l}O\\(OH)^4\end{array}\right.\\ C^6H\left\{\begin{array}{l}O\\CH^2.OH\end{array}\right.\end{array}$$

Salicin (glycosalicylalcohol).

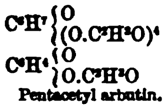


$$\begin{array}{l} C^6H^7\left\{\begin{array}{l}O\\(OH)^4\end{array}\right.\\ C^6H^4\left\{\begin{array}{l}O\\OH\end{array}\right.\end{array}$$

Arbutin (glycohydroquinone).

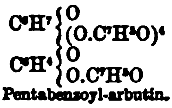
The hydrogen in the hydroxyls of the glucosic portion of arbutin may in fact be replaced by acid radicles, just as in the case of salicin (*Zeitschr.* [2] v. 1, 52); moreover, the hydrogen belonging to the hydroquinone in arbutin is easily replaceable, whereas in salicin the hydrogen belonging to the saligenin is not capable of substitution.

Benzoyl-arbutins are obtained by means of benzoyl chloride; *acetyl-arbutins*, with acetyl chloride or acetyl oxide, which act at 60°–80°. The ultimate products of the reaction separated from the resulting solutions, after cooling, by means of ether, contain free acid radicles, and have the following composition:



$$\begin{array}{l} C^6H^7\left\{\begin{array}{l}O\\(O.C^2H^3O)^4\end{array}\right.\\ C^6H^4\left\{\begin{array}{l}O\\O.C^2H^3O\end{array}\right.\end{array}$$

Pentacetyl arbutin.



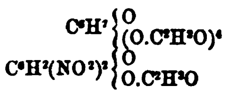
$$\begin{array}{l} C^6H^7\left\{\begin{array}{l}O\\(O.C^7H^5O)^4\end{array}\right.\\ C^6H^4\left\{\begin{array}{l}O\\O.C^7H^5O\end{array}\right.\end{array}$$

Pentabenzoyl-arbutin.

They are colourless bodies, insoluble in water, slightly soluble in ether, more soluble in hot alcohol, from which they crystallise on cooling in small shining needles. The acid radicles may easily be taken out again by boiling with weak bases. Together with the pentabenzoylated compound, Schiff likewise obtained *dibenzoyl-arbutin*, in which the hydrogen might be further replaced by acetyl.

Dinitro-arbutin dissolves easily in acetic oxide, and is converted into

Pentacetyl-dinitro-arbutin :



$$\begin{array}{r} C^6H^7\left\{\begin{array}{l}O\\(O.C^2H^3O)^4\end{array}\right.\\ C^6H^2(NO^2)^2\left\{\begin{array}{l}O\\O.C^2H^3O\end{array}\right.\end{array}$$

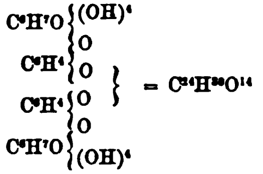
which may be separated from the acetic acid solution by water, and crystallised from hot alcohol in fine needles, insoluble in water, slightly soluble in ether. The alcoholic solution heated with sulphuric acid yields glucose, acetic ether, and dinitrohydroquinone, easily recognisable by the splendid colour which it gives with caustic alkalis. Dinitro-arbutin forms with basic lead acetate a crystalline orange-coloured lead-compound, in which the hydrogen of the hydroxyl is replaced by lead. Arbutin gives no precipitate, even with an ammoniacal solution of lead-acetate.

Recently precipitated silver oxide is reduced, even at ordinary temperatures, by an aqueous solution of arbutin. On adding freshly prepared silver carbonate to a solution of arbutin heated to 50°–60° as long as carbonic acid is evolved, and heating for a short time with excess of the silver carbonate, a yellow solution is obtained, which no longer contains arbutin; but on separating the dissolved silver with a few drops of hydrochloric acid, and filtering, a solution is obtained, from which alcohol precipitates white flocks consisting of a compound formed by the union of 2 mols. of arbutin minus 2 at. of hydrogen, viz.,

Diarbutin

or

Glycoquinhydrone



$$\left.\begin{matrix} C^6H^7O\left\{\begin{matrix}(OH)^4\\ O\end{matrix}\right. \\ C^6H^4\left\{\begin{matrix}O\end{matrix}\right. \\ C^6H^4\left\{\begin{matrix}O\\ O\end{matrix}\right. \\ C^6H^7O\left\{\begin{matrix}(OH)^4\end{matrix}\right. \end{matrix}\right\} = C^{24}H^{30}O^{14}$$

This compound may be regarded as the glucoside of quinhydrone (green hydroquinone); it is related to arbutin in the same manner as helicoidin to salicin. Glycoquinhydrone is not at all bitter; it forms acetyl-derivatives when treated with acetic oxide, and an orange-coloured nitro-product with nitric acid. The latter, when decomposed in alcoholic solution by sulphuric acid, does not yield any substance that turns violet with potash. By means of zinc and sulphuric acid, hydrogen may again be added, and dinitro-hydroquinone thereby produced (H. Schiff, *Zeitschr. f. Chem.* [2] v. 519).

ARBUTUS UNEDO. The ripe fruits of this tree contain a considerable quantity of inverted sugar, parapectin, a yellow waxy substance, a colouring matter which is turned violet by alkalis and yellow by acids; also metapectic acid and traces of starch (Filhol, *Compt. rend.* l. 1185).

ARCTUVIN. The name given by Kawalier to hydroquinone produced by the decomposition of arbutin (p. 191).

ARGENTACETYL-COMPOUNDS. Syn. with Argentovinyl-compounds. See Acetylene (p. 36).

ARGENTALLYLENE. See Allylene (p. 97).

ARGYRESCETIN
ARGYRESCIN } See Horse-chestnut (iii. 172).

ARIBINE. $C^{23}H^{20}N^4$.—A base extracted from the bark of *Araribra rubra*, a tree growing in Brazil. (See Additions, vol. v. p. 1087.)

ARKSUTITE. A fluoride occurring in Greenland together with cryolite. It is a white, highly lustrous, crystallo-granular mineral, having a sp. gr. of 3·029 to 3·175 and the hardness of cryolite. It gives by analysis 51·03 p. c. fluorine, 17·87 aluminium, 23·00 sodium, 7·01 lime, 0·57 water, and 0·74 insoluble matter (= 100·22), agreeing nearly with the formula $Al^2F^6.2(Ca;Na^2)F^2$ (Hagemann, *Sill. Am. J.* [2] xlii. 93).

ARNICA MONTANA. Both the root-stock and the flowers of this composite plant, which grows chiefly on upland meadows in the middle and south of Europe, are officinal. The root-stock has a faint aromatic odour, and a persistently sharp aromatic taste, slightly inclining to bitter. It contains resin, tannin, fat, colouring matter, and about 1 p. c. of a heavy yellowish volatile oil different from that which is contained in the flowers. According to Walz (*N. Jahrb. Pharm.* xiii. 175; *Jahresb.* 1860, p. 544), the oil from the root has the composition of hexyl caproate, $C^{12}H^{24}O^2$ or $C^6H^{13}.C^6H^{11}O^2$. The fat of the root contains, according to the same authority, a fatty acid, $C^{18}H^{28}O^2$, the magnesium salt of which may also be extracted from the leaves.

The flowers, which have a peculiar but not unpleasant odour, yield in the dry state from 1 to 2 tenths per thousand of volatile oil; in the fresh state a proportionally larger quantity. This oil has an acid reaction, a yellowish, bluish, or greenish colour, and smells like chamomile. Walz also found in the flowers two different resins, crystallisable fat and wax, tannin, and a yellow colouring matter.

The flowers, herb, and root of arnica contain also a yellow non-crystallisable bitter substance, which appears to be the active principle of the plant. This substance, arnicin, is easily soluble in ether, slightly soluble in water, and is precipitated from its alcoholic solution by tannin or by water; it has the characteristic odour and sharp taste of arnica. It is decomposed by dilute acids. Walz assigns to arnicin the formula $C^{20}H^{30}O^4$, which however requires confirmation. The flowers yield 1 p. c. less of it than the root-stock or the herb (Walz, *N. Jahrb. Pharm.* xiii. 175; xiv. 79; xv. 329; *Jahresb.* 1860, p. 544; 1861, p. 753).

According to Bastick (*J. Pharm.* [3] xix. 454), arnica flowers contain a non-volatile bitter alkaloïd, arnicine, which is soluble in alcohol and ether, very slightly soluble in water, decomposed by alkalis, but capable of forming crystallisable salts with acids. It was prepared by macerating the plant in alcohol acidulated with sulphuric acid, treating the solution with lime and afterwards with alkaline carbonates to separate resinous matters, agitating the filtrate with ether, and leaving the ethereal solution to evaporate.

Peretti (*Bull. della Correspondenza scient. di Roma*, 1861, No. 30) stated that arnica yields, by distillation with potash or lime, a peculiar volatile base; but Hesse (*Ann. Ch. Pharm.* cxxix. 254) has shown that the plant thus treated yields nothing but ammonia, with traces of trimethylamine.

AROMATIC SERIES. This term is applied to a group of compounds which range themselves round the hydrocarbons C^nH^{2n-6}. Originally given to the bodies of the benzoic group, on account of the aromatic odours possessed by some of them, as benzoic acid and bitter almond oil, it is now extended to several series of compounds homologous with these.

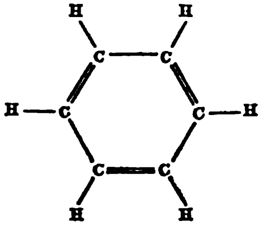
The aromatic compounds form a group running parallel, as it were, with the fatty bodies, and like the latter including hydrocarbons, alcohols, acids, amines, &c. They resemble the fatty bodies in many of their chemical relations, but they likewise exhibit decided peculiarities, which distinguish them from all other bodies and mark them as a natural family.

Transformations of fatty bodies into compounds belonging to the aromatic group by simple and definite reactions are not known to occur. It is true that particular aromatic bodies, as benzene and phenol, may be formed by the action of a strong heat on many compounds, and even very simple ones, belonging to the fatty series; but these are not, for the most part, simple metamorphoses in which the quantitative relations between the material and the product can be exactly estimated and the transformations represented by equations. On the other hand, aromatic substances when treated with powerful chemical reagents, especially oxidisers, frequently yield bodies belonging to the fatty series; but even in these cases there is always formed, in addition, at least one product belonging to the aromatic series, unless indeed a complete breaking up of the molecule takes place, resulting in the formation of the very simplest organic compounds, such as carbonic acid and oxalic acid.

To obtain an insight into the constitution of the aromatic bodies, the following facts must be taken into account.

The aromatic bodies are derived from the fundamental hydrocarbons, C^nH^{2n-6}, and the simplest of them are those which contain 6 atoms of carbon, or are derived from benzene, C^6H^6. Now these hydrocarbons are far from containing the maximum quantity of hydrogen required to saturate the *n* atoms of carbon contained in their molecules; in fact, if the carbon-atoms were united together in these molecules in the same manner as in the fatty series, the general formula of the saturated hydrocarbons would be C^nH^{2n+2}, and the compounds C^nH^{2n-6} would be octivalent radicles, capable of taking up 8, 6, 4, or 2 additional atoms of hydrogen or other monatomic element; and in fact they are capable, under certain circumstances, of uniting directly with chlorine, bromine, and other haloïd elements: thus benzene forms with chlorine a crystalline hexchloride, $C^6H^6Cl^6$. But in the greater number of their chemical relations, these hydrocarbons exhibit the characters of saturated molecules, which, like the paraffins, can take up other elements only in exchange for a part or the whole of their hydrogen.

To account for this property, Kekulé supposes* that the atoms of carbon in benzene, the fundamental hydrocarbon of the series, are united among themselves by one and two units of equivalence alternately, so that the constitution of this body is represented by the formula:



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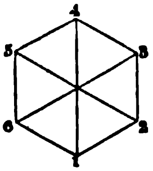
* *Lehrbuch der organischen Chemie*, ii. 496, et seq.

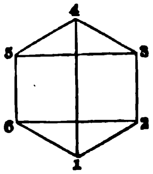
In the molecule thus represented, each of the carbon-atoms has all its four units of affinity satisfied, and the six carbon-atoms form, as it were, a closed chain or circle. We shall see in the sequel that from this formula of benzene the formulæ of nearly all the known bodies of the aromatic group can be formed by substitution, and that the formulæ thus obtained afford satisfactory explanations of the modes of formation and transformation, and of the isomeric relations of these bodies.

The sexvalent character of the benzene molecule might be explained by many other modes of linking together of the carbon-atoms, besides that proposed by Kekulé. Consider, for example, the modes of connection illustrated by the three following diagrams (the carbon-atoms being supposed to occupy the angles of the hexagon):

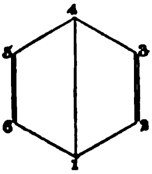
No. I.



No. II.

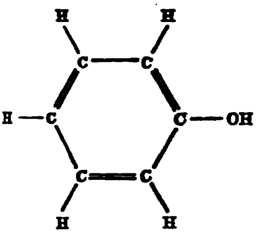


No. III.

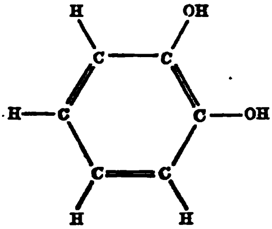


In the first and second of these modes of grouping, every carbon-atom is linked to three others, to each by one unit of affinity, and therefore, as in the arrangement previously considered, each has one unit free; in the third figure, the first and fourth carbon-atoms are linked to three others (two adjacent and one opposite), each by one unit of affinity, while the carbon-atoms 2, 3, 5, and 6 are each connected with two others, by one and by two units of affinity. The last arrangement differs therefore from the rest in not being symmetrical. It has been suggested as affording an explanation of a peculiar case of isomerism among the chlorinated derivatives of benzene, viz. the existence of two modifications of pentachlorobenzene, C^6HCl^5. Now according to the mode of linking of the carbon-atoms in Kekulé's diagram, or indeed in any other perfectly symmetrical arrangement, there should be but one such compound, inasmuch as the result must be the same whichever of the hydrogen-atoms of the benzene molecule is left in its place while the others are replaced by chlorine. But if we suppose the carbon-atoms to be linked as in diagram No. III. the properties of the molecule, C^6HCl^5, may be different accordingly as the remaining hydrogen-atom is situated, on the one hand, at 1 or 4, or, on the other, at 2, 3, 5, or 6. It must be observed, however, that the existence of the two modifications of pentachlorobenzene is not positively established, and, on the whole, the phenomena exhibited by aromatic bodies are best explained by supposing the carbon-atoms in the benzene molecule to be linked together symmetrically. The arrangements represented in the other two diagrams above given (Nos. I. and II.) exhibit this symmetry as well as that of Kekulé; but they do not explain so readily as the latter the formation of the additive compounds of benzene and the other aromatic hydrocarbons (p. 196) (Kekulé, *Deut. Chem. Gesells.* Berlin, 1869, p. 362).

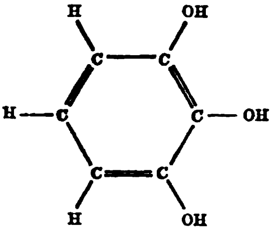
Benzene, the fundamental hydrocarbon of the aromatic group, gives rise to a numerous series of derivatives, by taking up other elements or compound radicles in exchange for one or more of its hydrogen-atoms. If the element which thus enters the molecule is monatomic, it simply takes the place of the hydrogen, satisfying the affinity of the carbon-atoms in the same way: thus, when benzene is acted upon by bromine or chlorine, one or more hydrogen-atoms are removed in the form of hydrobromic or hydrochloric acid, and bromobenzenes or chlorobenzenes are produced, viz. C^6H^5Br, $C^6H^4Br^2$, $C^6H^3Cl^3$, &c. But if the element which replaces the hydrogen is polyatomic, as O'', N''', or C^{iv}, only one of its units of affinity can be satisfied by combination with the unit of affinity of the carbon-atom which was previously satisfied by the displaced hydrogen, and consequently the polyatomic element can bring other atoms of hydrogen, or of equivalent elements or radicles, into the molecule to satisfy its remaining units of affinity. (See ATOMICITY.) Thus *oxygen*, which is diatomic or bivalent, brings with it one atom of hydrogen, the result being the same as if an atom of hydrogen in the benzene molecule were replaced by the univalent radicle hydroxyl, OH. The product thus formed is a phenol, monatomic, diatomic, or triatomic, according to the number of hydrogen-atoms replaced: thus



Phenol.

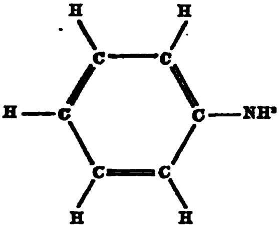


Hydroquinone.

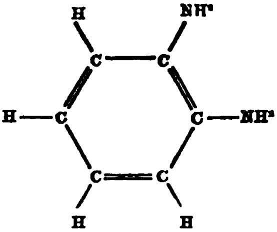


Pyrogallol.

In like manner, nitrogen, entering as a trivalent element, introduces two atoms of hydrogen, the result being the replacement of one or more atoms of hydrogen in the benzene molecule by amidogen, $(NH^2)'$. In this manner are formed from benzene, amidobenzene or aniline, $C^6H^5(NH^2)$, and diamidobenzene or phenylene-diamine, $C^6H^4(NH^2)^2$.

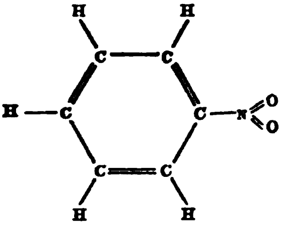


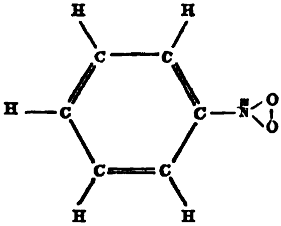
Aniline.



Phenylene-diamine.

In the nitrobenzenes the nitrogen may be supposed to enter either as a trivalent or as a quinquivalent element: thus mononitrobenzene, $C^6H^5(NO^2)$, may be represented by either of the following formulæ:

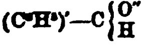




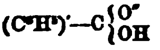
Lastly, *carbon*, which is quadrivalent, brings into the benzene molecule three atoms of hydrogen, the result being the replacement of one or more hydrogen-atoms in the benzene by the univalent radicle methyl, CH^3, or the addition of one or more equivalents of CH^3, whereby there is formed a series of hydrocarbons homologous with benzene: thus

C^6H^6	Benzene.
C^7H^8 or $C^6H^5(CH^3)$	Methyl-benzene or Toluene.
C^8H^{10} or $C^6H^4(CH^3)^2$	Dimethyl-benzene or Xylene.
C^9H^{12} or $C^6H^3(CH^3)^3$	Trimethyl-benzene.

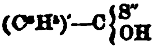
The three unattached units of affinity in the carbon-atom which enters the benzene-molecule may also be partly satisfied by a bivalent radicle, or wholly by a trivalent radicle, as in the following compounds:



$(C^6H^5)'\text{—}C\left\{\begin{matrix}O''\\H\end{matrix}\right.$ . . . . . . Benzoic aldehyde.



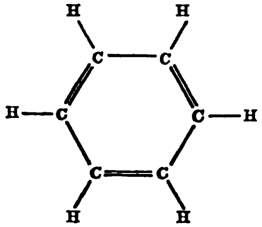
$(C^6H^5)'\text{—}C\left\{\begin{matrix}O''\\OH\end{matrix}\right.$ . . . . . . Benzoic acid.



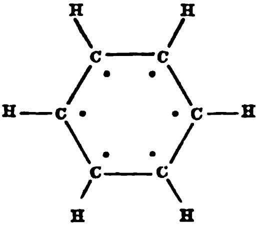
$(C^6H^5)'\text{—}C\left\{\begin{matrix}S''\\OH\end{matrix}\right.$ . . . . . . Thiobenzoic acid.

$(C^6H^5)'\text{—}CN'''$ . . . . . . Cyanobenzene or Phenyl cyanide.

Under certain circumstances also the aromatic hydrocarbons can take up other molecules by direct addition. Thus benzene, when subjected to the action of chlorine or bromine in sunshine, combines directly with those elements, forming the compounds $C^6H^6Cl^6$ and $C^6H^6Br^6$. In this case we may suppose that the chlorine or bromine acts in such a manner as to loosen the bonds of connection between some of the carbon-atoms, so that the atoms of the entire chain become united by one bond only, and each of them has one unit of affinity left free and ready to take up an atom of chlorine or bromine, thus (the dots in the second figure indicating unsaturated affinities):



Saturated.



Unsaturated.

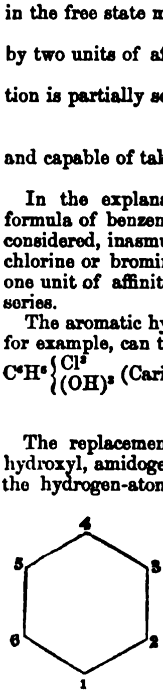
This partial separation of carbon-atoms, or opening out of the group, is not peculiar to the aromatic bodies, but frequently takes place in other series. Ethylene, for example, in the free state may be regarded as $\begin{array}{c}CH^2\\ \|\\ CH^2\end{array}$, its two carbon-atoms being linked together by two units of affinity; but under the influence of chlorine or bromine, the connection is partially severed, and the molecule becomes $\begin{array}{c}CH^2\\ |\\ CH^2\end{array}$, in which state it is bivalent, and capable of taking up 2 at. chlorine, forming the compound $\begin{array}{c}CH^2Cl\\ |\\ CH^2Cl\end{array}$.

In the explanation thus afforded of the formation of additive compounds, the formula of benzene proposed by Kekulé has the advantage of all the others above considered, inasmuch as if any one of the latter be adopted, we must suppose that chlorine or bromine can sever the connection between carbon-atoms united by only one unit of affinity, an effect of which no example has yet been observed in other series.

The aromatic hydrocarbons can also unite directly with *hypochlorous acid.* Benzene, for example, can take up 3 molecules of this acid, forming the crystalline compound $C^6H^6\left\{\begin{array}{l}Cl^3\\ (OH)^3\end{array}\right.$ (Carius, *Ann. Ch. Pharm.* cxxvi. 195; cxxxvi. 324).

Isomerism in the Aromatic Series.

The replacement of one atom of hydrogen in benzene by chlorine, bromine, hydroxyl, amidogen, methyl, &c., must evidently yield the same result, whichever of the hydrogen-atoms may be thus replaced, inasmuch as the molecule is perfectly symmetrical. Accordingly there is but one monochlorinated or monobrominated benzene, one monatomic alcoholic derivative, viz. phenol, $C^6H^5(OH)$, one monatomic amidated derivative, viz. aniline, $C^6H^5(NH^2)$, one monomethyl derivative, viz. toluene, $C^6H^5(CH^3)$, &c.



But when two or more atoms of hydrogen in the benzene molecule are thus replaced, isomeric modifications become possible, accordingly as the elements or radicles which take the place of the hydrogen are contiguous, or are separated from one another by smaller or larger intervals. This will be more clearly understood if we represent the molecule of benzene by a hexagon, the six angles of which are occupied by the hydrogen-atoms numbered from 1 to 6. It will then be seen that the derivatives formed by successive substitution exhibit the following modifications:

a. The hydrogen-atoms are successively replaced by the same element or compound radicle (lateral chain). In this case the number of modifications is as follows:—

	Number of hydrogen-atoms replaced	Number of modifications	Places of the replaced H-atoms		
a	one	one	1		
b	two	three	1,2	1,3	1,4
c	three	three	1,2,3	1,2,4	1,3,5
d	four	three	1,2,3,4	1,2,4,5	1,3,4,5
e	five	one	1,2,3,4,5		
f	six	one			

b. The hydrogen-atoms are replaced by different elements or radicles.

If only two hydrogen-atoms are thus replaced, the number of possible modifications remains the same as above, viz. three: for the reversal of the order (AB or BA) can make no difference in the result.

But if three or more hydrogen-atoms are replaced by different radicles, the number of possible modifications becomes larger, inasmuch as the order of succession of the radicles introduced by substitution may then exert an influence on the nature of the product. Thus for a benzene-derivative represented by the general formula $C^6H^3A^2B$ we find:

α,	corrresponding to	1, 2, 3 (see c above);	C^6H^3AAB C^6H^3ABA
β,	„	1, 2, 4 („);	C^6H^2AHAB C^6H^2AHBA C^6H^3BHAA
γ,	„	1, 3, 5 („);	$C^6HAHAHB$ $C^6HAHBHA$ $C^6HBHAHA$

In the present state of our knowledge, we cannot in all cases assign to the several radicles which replace the hydrogen in benzene their exact relative positions in each isomeric modification; but, inasmuch as a given modification of a benzene-derivative may in many cases be converted by simple metamorphoses into a particular modification of another benzene-derivative, we may conclude that in the two derivatives thus producible one from the other, the radicles which have replaced two or more atoms of hydrogen occupy corresponding places. Accordingly, the derivatives of benzene containing a given number of replaced hydrogen-atoms may be divided into groups, each containing those modifications which can be formed one from the other, and in which, therefore, the radicles which have replaced the hydrogen-atoms may be supposed to be similarly situated.

The bi-derivatives of benzene, e.g. bichlorobenzene, C^6H^4ClCl, chlorobromobenzene, C^6H^4ClBr, chlorophenol, $C^6H^4Cl(OH)$, chlorobenzoic acid, $C^6H^4Cl(CO^2H)$, &c., may be divided into three such groups, in which the radicles replacing the two hydrogen-atoms occupy the places (1 : 2), (1 : 3), and (1 : 4) respectively, or, in other words, are placed contiguously, or separated by one or by two atoms of hydrogen.[*] Chlorobromobenzene, for example, exhibits the three following modifications:

$C^6HHHHClBr$	$C^6HHHClHBr$	$C^6HHClHHBr$
1 : 2	1 : 3	1 : 4

the hydrogen-atoms in the benzene molecule $C^6HHHHHH$ being numbered from right to left.

Similar examples are afforded by the three diatomic phenols $C^6H^4\left\{\begin{matrix}OH\\OH\end{matrix}\right.$, viz. hydroquinone, pyrocatechin, and resorcin; the three modifications of the acid $C^6H^4\left\{\begin{matrix}OH\\CO^2H\end{matrix}\right.$, viz., oxybenzoic acid, salicylic acid, and para-oxybenzoic acid; and those of the amidated acid $C^6H^4\left\{\begin{matrix}NH^2\\CO^2H\end{matrix}\right.$, viz., amidobenzoic acid, amidosalylic or anthranilic acid, and amidodracylic acid.

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[*] It is clear that these are all the possible arrangements, inasmuch as (2 : 3), (3 : 4), (4 : 5), (5 : 6), and (6 : 1) are identical with (1 : 2); (2 : 4), (3 : 5), and (4 : 6) with (1 : 3); (2 : 5) and (3 : 6) with (1 : 4).

The manner in which the members of a particular group are producible one from the other may be illustrated by the following examples:

Iodaniline prepared from nitro-iodobenzene is converted by treatment with nitrous acid, into diazo-iodobenzene, $C^6H^3N^2I$, from which, by boiling its sulphate with water, iodophenol, $C^6H^4I(OH)$, is produced; and this, when fused with potash, is converted by exchange of I for OH into hydroquinone, $C^6H^4(OH)^2$. From the same diazo-iodobenzene may also be obtained di-iodobenzene, $C^6H^4I^2$, chloriodobenzene, C^6H^4ClI, and bromiodobenzene. All these derivatives of benzene belong to the same group, the replacement of the hydrogen in them occurring in corresponding places. The nitraniline * obtained from nitrated anilides (iv. 445) yields a diazo-derivative, the decomposition of which yields the same nitro-iodobenzene as that above mentioned; it therefore belongs to the same series. Moreover, since chloraniline and bromaniline are evidently analogous to iodaniline, and their generators, nitrochlorobenzene and nitro-bromobenzene, are analogous to nitro-iodobenzene, these bodies, and therefore also all bi-derivatives of benzene which can be obtained from them by simple transformation, belong to the same series: consequently, diazochlorobenzene, dichlorobenzene, chlorobromobenzene, diazobromobenzene, and dibromobenzene. To the same group belong nitrobenzoic acid, formed by the action of fuming nitric acid on benzoic acid; amidobenzoic acid, obtained from it by reduction; and oxybenzoic acid, formed from the latter by the action of nitrous acid. This series of bi-derivatives of benzene is called the *Ortho-* series.

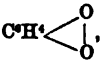
A second series of bi-derivatives of benzene—the *Para-* series—is produced from dinitrobenzene. From this compound is obtained *para-nitraniline*,† which may be converted into para-diazonitrobenzene, and from this may be prepared parachloronitrobenzene, parabromonitrobenzene, and para-iodo-nitrobenzene. These last compounds may be converted by reducing agents into parachloraniline, parabromaniline, and para-iodaniline, which again may be converted into the corresponding paradiazobenzenes. The paradiazo-iodobenzene thus obtained is converted by decomposing its sulphate with water into para-iodophenol, which when fused with potash yields resorcin, $C^6H^4(OH)^2$, isomeric with hydroquinone. In all these bi-derivatives of benzene the substitution evidently takes place in corresponding parts of the molecule. To the same series belong paranitrobenzoic or nitrodracylic acid, formed by oxidation of bromotoluene; also its reduction-derivative, amidodracylic acid, and paraoxybenzoic acid, produced from the latter by the action of nitrous acid (iv. 353).

The third series of bi-derivatives of benzene—the *Meta-* series—includes salicylic acid and its derivatives, chlorosalylic, amidosalylic, or anthranilic acid; also an iodophenol different from para- or ortho- iodophenol, formed, together with the latter, by treating phenol with iodine and iodic acid, and converted by fusion with potash into pyrocatechin.

The question as to the relative positions of the radicles in these three groups of compounds—whether, for example, the arrangement 1 : 2 exists in the ortho-, the meta-, or the para- series, has lately been the subject of considerable discussion, and may now be regarded as at least approximately settled.

Phthalic acid, $C^6H^4\left\{\begin{matrix}CO^2H\\CO^2H\end{matrix}\right.$, is formed by oxidation of naphthalene, $C^{10}H^8 = C^6H^4(C^4H^4)$, two of the four groups CH being completely eliminated from the molecule in the form of carbon dioxide and water, while the two others remain in the form of carboxyl, CO^2H:

$$C^6H^4(C^4H^4) + O^9 = 2CO^2 + H^2O + C^6H^4\left\{\begin{matrix}CO^2H\\CO^2H\end{matrix}\right..$$

Now, from the structure of the molecule of naphthalene, as recently determined by Graebe (p. 212), it appears most probable that the two groups CH thus oxidised to CO^2H occupy contiguous places; that is to say, the positions 1 : 2. But nitrophthalic acid is converted by reduction with tin and hydrochloric acid into amidobenzoic acid, which, when treated with nitrous acid yields oxybenzoic acid, and these compounds belong to the ortho- group. In this group, therefore, the radicles which replace two of the hydrogen-atoms of the benzene molecule occupy contiguous places, that is 1 : 2. This conclusion is corroborated by the constitution of hydroquinone, $C^6H^4\left\{\begin{matrix}OH\\OH\end{matrix}\right.$, which is formed from ortho-iodophenol, and is converted by oxidation into quinone,  $C^6H^4\langle O_2$, whereas its isomerides, pyrocatechin and resorcin, do not yield quinone by oxidation; this difference of reaction points to the conclusion that the two groups OH are contiguous in hydroquinone, and not in its two isomerides. (See QUINONE.)

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* Hofmann's β-nitraniline (iv. 445).

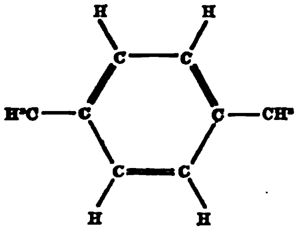
† Hofmann's α-nitraniline (iv. 445).

Baeyer has shown (*Ann. Ch. Pharm. Suppl.* v. 79) that mesitylene, C^9H^{12}, is a symmetrically constituted trimethyl-benzene, $C^6H^3(CH^3)^3$, that is to say that the three methyl-groups contained in it are separated by equal intervals, or occupy the positions 1, 3, 5. Consequently in isoxylene or dimethyl-benzene, $C^6H^4(CH^3)^2$, which is formed from it (from mesitylenic acid), the two methyl-groups must be separated by one interval, or occupy the places 1, 3. Now isoxylene is converted by oxidation into isophthalic acid, $C^6H^4(CO^2H)^2$, in which therefore the two groups CO^2H occupy the positions 1, 3. Hence for the third modification of the acid, $C^6H^4(CO^2H)^2$, or terephthalic acid, there remains only the arrangement 1, 4. But terephthalic acid belongs to the para- series, being formed from bromotoluene, $C^6H^4Br(CH^3)$, which is convertible by oxidation into parabromobenzoic or bromodracylic acid. In the para- series, therefore, the elements or radicles which replace the hydrogen-atoms occupy the positions 1, 4; so that for the meta- series there remains only the position 1, 3. The principal representatives of the three series are the following:

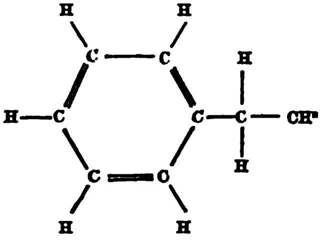
Ortho 1, 2	Meta 1, 3	Para 1, 4
Hydroquinone.	Pyrocatechin.	Resorcin.
Oxybenzoic acid.	Salicylic acid.	Para-oxybenzoic acid.
Phthalic acid.	Isophthalic acid.	Terephthalic acid.

Further developments of these views will be given in connection with the individual compounds of the aromatic series. See especially BENZENE, HOMOLOGUES OF, and BENZOIC ACID.

The bodies of the aromatic series exhibit also another kind of isomerism distinct from that above described. Consider first the hydrocarbons. Benzene and toluene are not susceptible of isomeric modifications: for the first is perfectly symmetrical, and in the formation of the second, or methyl-benzene, $C^6H^5(CH^3)$, the substitution of methyl for hydrogen may take place indifferently in any part of the molecule. But any further substitution of methyl for hydrogen may be made either within the phenyl-group C^6H^5, or in the methyl-group CH^3, and the result will not be the same in the two cases; hence the hydrocarbon C^8H^{10} exhibits the two modifications, dimethyl-benzene or xylene, $C^6H^4(CH^3)^2$, and ethyl-benzene, $C^6H^5(C^2H^5)$:



Dimethyl-benzene.



Ethyl-benzene.

In molecules thus constituted, the six carbon-atoms of the benzene group, with their accompanying hydrogen-atoms, are said to form the principal chain, while the alcohol-radicles or their modifications substituted for any of these hydrogen-atoms constitute lateral chains; thus methyl-benzene and ethyl-benzene have each only one lateral chain, whereas dimethyl-benzene has two.

The constitution of these hydrocarbons is determined: *a. By synthesis.*—Thus toluene is produced by the action of sodium on a mixture of bromobenzene and methyl-iodide: hence it has the constitution of methyl-benzene:

$$C^6H^5Br + CH^3I + Na^2 = NaBr + NaI + C^6H^5.CH^3.$$

Ethyl-benzene is formed in like manner from bromobenzene and ethyl-iodide. Xylene, which is a constituent of light coal-naphtha, is produced synthetically by the action of sodium on a mixture of bromo-toluene and methyl-iodide; hence it consists of methyl-toluene or dimethyl-benzene:

$$C^6H^4Br.CH^3 + CH^3I + Na^2 = NaBr + NaI + C^6H^4(CH^3)^2.$$

β. By oxidation.—Methyl-benzene and ethyl-benzene both yield by oxidation benzoic acid, $C^6H^5.CO^2H$, which, like these hydrocarbons themselves, contains only one lateral chain; but dimethyl-benzene (xylene) and methyl-ethyl-benzene, when oxidised with dilute chromic acid, yield terephthalic acid, $C^6H^4\left\{\begin{matrix}CO^2H\\CO^2H\end{matrix}\right.$, which contains two lateral chains. Hence it is inferred that the acid or acids produced by the oxidation of an aromatic hydrocarbon contain as many lateral chains as the hydrocarbon itself. This law affords the means of determining the constitution of certain aromatic hydrocarbons which have not yet been formed synthetically, as in the following cases:

The hydrocarbon C^9H^{12} exhibits the three following modifications:

$C^6H^5(C^3H^7)$	$C^6H^4(CH^3)(C^2H^5)$	$C^6H^3(CH^3)^3$
Propyl-benzene.	Methyl-ethyl-benzene.	Trimethyl-benzene.

All three have been prepared synthetically: the first, by the action of sodium on a mixture of monobromobenzene and normal propyl-iodide; the second, in like manner from monobromo-toluene and ethyl-bromide; the third, from monobromoxylene and methyl-iodide. This last compound, also called *coal-tar cumene* or *pseudocumene*, exists in coal-tar oil, and is obtained therefrom by fractional distillation; it boils at about 166°; methyl-ethyl-benzene at 159°; propyl-benzene at 157°. Coal-tar cumene is not however a perfectly definite substance, but a mixture of three isomeric modifications of trimethyl-benzene differing from one another in the relative position of the methyl-atoms. (See BENZENE, HOMOLOGUES OF.) Cumene produced by distilling cumic acid with excess of lime boils at 151°–151·5°, and is therefore different from either of the preceding compounds. Nevertheless, it agrees with propyl-benzene, $C^6H^5.CH^2CH^2CH^3$, in yielding only benzoic acid by oxidation, and therefore contains but one lateral chain: hence it may be supposed to consist of isopropyl-benzene, $C^6H^5.CH(CH^3)^2$, a view of its constitution which is in accordance with its lower boiling point; but isopropyl-benzene has not yet been prepared synthetically (Fittig, Schäffer a. König, *Ann. Ch. Pharm.* cxlix. 324). All the higher aromatic hydrocarbons containing the radicle C^3H^7 are susceptible of similar modifications.

The following table exhibits the metameric modifications of all the aromatic hydrocarbons, C^nH^{2n-6}, at present known:

C^6H^6 Benzene.				
C^7H^8	$C^6H^5(CH^3)$ Methyl-benzene * (toluene).			
C^8H^{10}	$C^6H^5(CH^2CH^3)$ Ethyl-benzene.*	$C^6H^4(CH^3)^2$ Methyl-toluene * (xylene).		
C^9H^{12}	$C^6H^5(C^3H^7)$ Propyl-benzene * (cumene).	$C^6H^4\left\{\begin{matrix}CH^3\\C^2H^5\end{matrix}\right.$ Ethyl-toluene.*	$C^6H^3(CH^3)^3$ Trimethyl-benzene * (pseudocumene).	
$C^{10}H^{14}$		$C^6H^4\left\{\begin{matrix}CH^3\\C^3H^7\end{matrix}\right.$ Methyl-propyl-benzene * (α cymene).	$C^6H^3\left\{\begin{matrix}(CH^3)^2\\C^2H^5\end{matrix}\right.$ Ethyl-xylene.*	$C^6H^2(CH^3)^4$ β cymene (from coal-tar).
$C^{11}H^{16}$	$C^6H^5(C^5H^{11})$ Amyl-benzene.*		$C^6H^3\left\{\begin{matrix}CH^3\\(C^2H^5)^2\end{matrix}\right.$ Diethyl-xylene (laurene).	
$C^{12}H^{18}$		$C^6H^4\left\{\begin{matrix}CH^3\\C^5H^{11}\end{matrix}\right.$ Amyl-toluene.		
$C^{13}H^{20}$			$C^6H^3\left\{\begin{matrix}(CH^3)^2\\C^5H^{11}\end{matrix}\right.$ Amyl-xylene.*	

* The hydrocarbons with asterisks attached to their names are those which have been formed synthetically,

The constitution of these hydrocarbons is determined on the principles above explained. Some of them, viz. dimethyl-benzene and trimethyl-benzene, are also known to exhibit isomeric modifications depending on the relative position of the methyl-atoms. Their modes of formation and properties will be described in detail in the article BENZENE, HOMOLOGUES OF.

The hydrocarbon C^8H^6, formed by abstraction of 2HCl from methyl-benzylal chloride, $C^8H^8Cl^2$ (with alcoholic potash), and in other ways (p. 5), is also related to the aromatic group, though it does not belong to the homologous series C^nH^{2n-6}, having the composition of acetenyl-benzene, $C^6H^5(C^2H)$.

The derivatives of toluene and its higher homologues, formed by replacing one or more atoms of hydrogen with chlorine, bromine, hydroxyl, amidogen, &c., likewise exhibit the isomerism or metamerism just noticed in the hydrocarbons, depending upon the position of the substituted radicle in the principal or in one or more of the lateral chains. Thus toluene or methyl-benzene, $C^6H^5.CH^3$, forms two monochlorinated derivatives, viz.,

$C^6H^4Cl.CH^3$	and	$C^6H^5.CH^2Cl$
Chlorotoluene		Benzyl chloride,

and three dichlorinated derivatives, viz.,

$C^6H^3Cl^2.CH^3$	$C^6H^4Cl.CH^2Cl$	$C^6H^5.CHCl^2$
Dichlorotoluene	Chlorobenzylic chloride	Chlorobenzol,

and the higher derivatives admit of still more numerous modifications. Similarly with the bromides and iodides. (See TOLUENE, v. 852.)

Those derivatives in which the substitution of the chlorine, &c., takes place in the lateral chains are altogether more active compounds than those in which it takes place in the principal chain. It fact, the chlorine in such a compound as benzyl chloride, $C^6H^5.CH^2Cl$, occupies a position similar to that which it takes up in the chlorinated compounds of the fatty series, so that the compound in question is an alcoholic chloride, capable of readily exchanging its chlorine for other radicles by double decomposition, and being thereby converted into the corresponding alcohol, amine, ethers, &c. On the other hand, the chlorine or other haloïd element which takes the place of hydrogen in the principal chain, as in chlorotoluene, $C^6H^4Cl.CH^3$, dichlorotoluene, $C^6H^3Cl^2.CH^3$, &c., is more surrounded by carbon-atoms, like the chlorine-atoms in the corresponding derivatives of benzene itself; and under these circumstances the compound is found to be more stable, the chlorine, bromine, &c., showing but little tendency to separate from it by double decomposition; in other words, the compounds in question do not exhibit the characters of alcoholic chlorides.

In like manner, toluene yields two derivatives by substitution of one atom of *hydroxyl* for hydrogen, viz.,

$C^6H^5.CH^2OH$	$C^6H^4(OH).CH^3$
Benzyl alcohol.	Cresol.

The first of these compounds, and its homologues, xylyl alcohol, $C^7H^7.CH^2OH$, &c., are true alcohols, resembling the primary alcohols of the fatty series in having two atoms of hydrogen in immediate connection with the group OH, and being consequently capable of yielding by oxidation the corresponding aldehydes and acids. But cresol and its homologues, in which the hydroxyl enters into the principal chain, are not true alcohols, but phenols, homologous with the typical 6-carbon phenol, $C^6H^5(OH)$, and, like that compound, not convertible by oxidation into aldehydes and acids of analogous constitution.

The phenols further differ from the true alcohols in the following respects: 1. They are not converted into ethers by the action of acids. The 6-carbon phenol, for example, does not yield phenyl chloride or monochlorobenzene, C^6H^5Cl, by distillation with strong hydrochloric acid, but only when subjected to the action of phosphorus pentachloride: in like manner, to obtain phenyl benzoate, $C^6H^5.C^7H^5O^2$, phenol must be distilled, not with benzoic acid, but with benzoic chloride (iv. 390).—2. The true alcohols when treated with *nitric acid* are either oxidised to aldehydes and acids, or converted into nitric ethers, which are neutral, and may be saponified by alkalis like other compound ethers, reproducing the acid and the alcohol. But the phenols, under the influence of nitric acid, yield products in which not merely one, but two or three atoms of hydrogen may be replaced by nitryl, NO^2, the products possessing decided acid properties, and not being saponifiable, like compound ethers.—3. The phenols treated with *chlorine* yield substitution-products in which 1, 2, or 3 atoms of hydrogen are replaced by chlorine.—4. The phenols have a much more decidedly acid character than the true alcohols, forming salts with alkaline hydrates by double decomposition, a reaction exhibited only exceptionally by true alcohols.—5. The phenates of alcohol-radicles, such as methyl phenate or anisol, $C^6H^5(CH^3)O^2$, differ from mixed ethers (like methyl ethylate, $C^2H^5(CH^3)O$) in this respect, that under the influence of powerful reagents, such as nitric acid, they yield a single product—anisol for instance, when treated with nitric acid yielding nitranisol, dinitranisol, or trinitranisol—whereas the mixed ethers split up under similar circumstances, yielding compounds corresponding to each of the alcohol-radicles which they contain.

The following table exhibits the formulæ of the known monatomic hydroxyl derivatives of the aromatic series, together with the hydrocarbons from which they are derived:

Hydrocarbons.	*Alcohols.*	*Phenols.*
C^6H^6 Benzene.	———	$C^6H^5(OH)$
$C^6H^5.CH^3$ Methyl-benzene or Toluene.	$C^6H^5.CH^2(OH)$ Benzyl alcohol.	$C^6H^4(OH).CH^3$ Cresol.
$C^6H^5.CH^2CH^3$ Ethyl-benzene.	———	$C^6H^4(OH).CH^2CH^3$ Ethyl-phenol or Phlorol.
$C^6H^4.(CH^3)^2$ Dimethyl-benzene or Xylene.	$C^6H^4.CH^3.CH^2(OH)$ Xylyl alcohol.	$C^6H^3(OH).(CH^3)^2$ Dimethyl-phenol.
$C^6H^4.CH^3.C^3H^7$? Cymene.	$C^6H^4.C^3H^7.CH^2OH$ Cymyl alcohol.	———
$C^6H^4.(C^2H^5)^2$ Diethyl-benzene.	———	$C^6H^3(OH).(C^2H^5)^2$ Thymol.
$C^{17}H^{28}$ Sycocerene.	$C^{17}H^{27}(OH)$ Sycoceryl alcohol.	———

The replacement of two hydrogen-atoms in toluene by hydroxyl may give rise to three isomeric diatomic alcohols:

$$C^6H^5.CH(OH)^2; \qquad C^6H^4(OH).CH^2(OH); \qquad C^6H^3(OH)^2.CH^3.$$

The first of these, which has not yet been obtained, has the constitution of a glycol: the second, which is saligenin (v. 172), possesses an alcoholic and a phenolic hydroxyl, and may accordingly be called a glycophenol: it is intermediate in its properties between the alcohols and the phenols, being converted, on the one hand, into the corresponding aldehyde, viz. salicylol, $C^7H^6O^2$, by the action of chromic acid and other oxidising agents, and on the other, into benzoyl-salicin, $C^7H^7(C^7H^5O)O^2$, by the action of benzoyl chloride (v. 173). The third of the above formulæ, $C^6H^3(OH^2).CH^3$, is that of a diatomic phenol, and probably represents the constitution of orcin.

The following table exhibits the composition of the diatomic hydroxyl derivatives of benzene at present known:

Hydroquinone (1 : 2) . . Oxyphenol or Pyrocatechin (1 : 3) Resorcin (1 : 4) . . .	$C^6H^6O^2 = C^6H^4(OH)^2$
Saligenin	$C^7H^8O^2 = C^6H^4(OH).CH^2(OH)$
Orcin . . . . . Guaiacol (in part) . .	$C^7H^8O^2 = C^6H^3(OH)^2.CH^3$
Creosol . . . . Veratrol	$C^8H^{10}O^2 = C^8H^8(OH)^2$

The three modifications of the 6-carbon diatomic phenol are produced, as above mentioned (p. 198), by the action of fusing caustic potash on the three corresponding modifications of iodophenol:

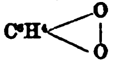
$$C^6H^4I(OH) + KOH = KI + C^6H^4(OH)^2.$$

Pyrocatechin is also formed by heating oxysalicylic acid, $C^7H^6O^4$, just as phenol is produced fron salicylic acid, $C^7H^6O^3$. In like manner orcin is produced from orsellinic acid, $C^8H^8O^4$, and veratrol from veratric acid, $C^9H^{10}O^4$. Saligenin is formed from its aldehyde, salicylol, $C^7H^6O^2$, by the action of nascent hydrogen, also by the action of acids or of emulsin on salicin. Guaiacol and creosol are obtained from guaiacum; the latter also from beech-tar creosote.

Intimately connected with the diatomic phenols are the quinones, which are compounds derived from the aromatic hydrocarbons by substitution of O^2 for H^2, the two atoms of oxygen thus introduced being linked together by one of their affinities so as to form a bivalent group or radicle: thus,

C^6H^6

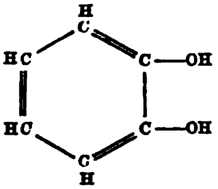
Benzene.

 or $C^6H^4(O^2)''$.

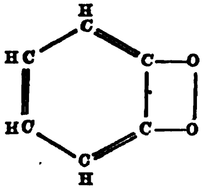
Quinone.

$C^6H^5.CH^3$ Toluene. $C^6H^3(O^2)''.CH^3$ Toluquinone.

Quinone, $C^6H^4O^2$, is formed by oxidation of hydroquinone, $C^6H^4(OH)^2$, the two hydrogen-atoms of the hydroxyl being removed and the two oxygen-atoms then uniting together; thus:



Hydroquinone.



Quinone.

Pyrocatechin and resorcin are not converted by oxidation into quinone; this difference affords a confirmation of the view that in hydroquinone the two hydroxyl groups are contiguous, whereas in pyrocatechin and resorcin they are separated and occupy the relative positions 1, 3 and 1, 4.

Of triatomic phenols, three bodies are known, having the composition $C^6H^6O^3 = C^6H^3(OH)^3$, viz. *pyrogallol* or *pyrogallic acid*, *phloroglucin* and *frangulin*. (See the several articles in the Dictionary.)

The amidated derivatives of toluene, viz.,

$C^6H^5.CH^2(NH^2)$ Benzylamine $C^6H^4(NH^2).CH^3$ Toluidine,

exhibit differences of character similar to those of the hydroxyl derivatives above considered, according to the position occupied by the amidogen. Benzylamine is a much stronger base than toluidine; resembles the bases of the fatty series in its reactions; and, like those bases, may be produced, together with di- and tri-benzylamine, by heating benzyl chloride with ammonia; whereas toluidine is not producible by any such reaction, but only by the action of reducing agents on nitrotoluene, in the same manner as aniline, of which it is the true homologue, is formed from nitrobenzene. (For details respecting these compounds, see vol. v. p. 865–868; also the articles BENZYLAMINE and TOLUIDINE in this volume.)

Toluidine admits of three modifications according to the relative positions of the groups NH^2 and CH^3, and two of these (ortho and para) one crystalline, the other liquid, are actually known, being obtained by reduction of the corresponding nitrotoluenes.

Xylidine, $C^8H^9(NH^2)$, *cumidine*, $C^9H^{11}(NH^2)$, and *cymidine*, $C^{10}H^{13}(NH^2)$, are of course susceptible of a larger number of modifications. Two modifications of xylidine have been obtained, but the higher bases are known only in one form.

The aromatic acids also exhibit metameric modifications accordingly as the radicle COOH replaces a hydrogen-atom in the principal or in the lateral chains. This kind of isomerism is exhibited in the first instance by toluic acid, $C^8H^8O^2$ (benzoic acid, $C^7H^6O^2 = C^6H^5.CO^2H$, does not admit of isomeric modifications), which may be derived from the hydrocarbon C^8H^{10} by substitution of O(OH) for H^3. Now, the hydrocarbon itself exists in the two modifications, dimethyl-benzene or xylene, $C^6H^4.(CH^3)^2$, and ethyl-benzene, $C^6H^5.CH^2CH^3$. Making the substitution just mentioned in these two formulæ, we obtain the two acids:

$C^6H^4\left\{\begin{matrix}CH^3\\COOH\end{matrix}\right.$ Toluic acid. $C^6H^5.CH^2COOH$ α-toluic acid.

The constitution of these two acids is shown by their synthetical formation, the first being produced (as a sodium-salt) by the action of sodium and carbon dioxide on bromotoluene (Kekulé, *Bull. Soc. Chim.* 1866, ii. 47):

$$C^6H^4Br.CH^3 + Na^2 + CO^2 = NaBr + C^6H^4\left\{\begin{matrix}CH^3\\CO^2Na\end{matrix}\right.;$$

the second by the hydration of benzyl cyanide (Cannizzaro, *Ann. Ch. Pharm.* xcvi. 216):

$$C^6H^5.CH^2CN + 2H^2O = NH^3 + C^6H^5.CH^2CO^2H.$$

The diatomic and monobasic acids of the series exhibit the same cases of isomerism as the monatomic acids. Thus to the two toluic acids above mentioned there should correspond the two diatomic acids:

$$C^6H^3OH\left\{\begin{matrix}CH^3\\COOH\end{matrix}\right. \text{ and } C^6H^4OH.CH^2COOH.$$

But further cases of isomerism arise from the circumstance that the non-acid hydroxyl in each of these acids may be either alcoholic or phenic. Hence each of the oxytoluic acids just formulated may have two isomeric forms, viz.,

$$C^6H^3OH\left\{\begin{matrix}CH^3\\COOH\end{matrix}\right. \text{ and } C^6H^4\left\{\begin{matrix}CH^2OH\\COOH\end{matrix}\right. .$$

$$C^6H^4OH.CH^2COOH \text{ and } C^6H^5.CHOH.COOH.$$

Two of these four possible isomers are actually known, viz.,

Cresotic acid . . . . $C^6H^3OH\left\{\begin{matrix}CH^3\\COOH\end{matrix}\right.$

Formobenzoic acid . . $C^6H^5.CHOH.COOH.$

Salicylic acid, $C^6H^4OH.CO^2H$, phloretic acid, $C^8H^8OH.CO^2H$, and thymotic acid, $C^{10}H^{12}OH.CO^2H$, resemble cresotic acid in containing a phenic hydroxyl. Formobenzoic acid has at present no known homologues.

Formation of Aromatic Compounds.

I. Of Hydrocarbons.—Benzene is produced by the union of three molecules of acetylene, C^2H^2, into one (p. 32), and may therefore be regarded as ultimately formed by the direct union of carbon and hydrogen. The other aromatic hydrocarbons are produced synthetically, as already observed, by the action of sodium on mixtures of their brominated derivatives with alcoholic iodides or bromides (p. 199). Each hydrocarbon of the series is also formed on distilling the aromatic acid containing one more atom of carbon than itself with lime, which abstracts carbon dioxide:

$$\underset{\text{Acid.}}{C^{n+1}H^{2n-6}O^2} = CO^2 + \underset{\text{Hydrocarbon.}}{C^nH^{2n-6}}$$

Benzene and its methylated derivatives are also produced in the destructive distillation of organic bodies, and are found especially in coal-tar, but the manner in which they are formed in these processes is not completely understood. (See HYDROCARBONS.)

II. Of Aromatic Alcohols and Phenols.—Benzyl alcohol and its homologues may be obtained from the corresponding hydrocarbons by replacing 1 at. hydrogen in these latter by chlorine, treating the chlorinated product with silver acetate, and saponifying the acetic ether with potash (Cannizzaro, *Ann. Ch. Phys.* [3] xlv. 468). This method is identical with that by which the fatty alcohols are obtained from the paraffins; but in the case of the aromatic bodies it is important to observe that the action of the silver acetate on the chlorinated compound takes place only when the chlorine is situated in one of the lateral chains (p. 199).

The aromatic alcohols are likewise produced by fixation of hydrogen upon the corresponding aldehydes, e.g. benzyl alcohol, C^7H^8O, from benzoic aldehyde, C^7H^6O. This fixation of hydrogen may be effected, as in the fatty series, by means of sodium amalgam; but it may also be effected by another process, peculiar to the aromatic series, viz. by the action of alcoholic potash on the aldehydes (Cannizzaro, *Ann. Ch. Phys.* [3] xl: 234): e.g.,

$$\underset{\substack{\text{Benzoic}\\\text{aldehyde.}}}{2C^7H^6O} + \underset{\text{Potash.}}{KOH} = \underset{\substack{\text{Potassium}\\\text{benzoate.}}}{C^7H^5KO^2} + \underset{\substack{\text{Benzyl}\\\text{alcohol.}}}{C^7H^8O}$$

The phenols are produced synthetically: *a.* By converting the hydrocarbons into the corresponding amines by Zinin's process; subjecting the nitrates of these bases in aqueous solution to the action of nitrous acid; and boiling the resulting diazo-compounds with water, whereby nitrogen is evolved, and a phenol is produced: e.g.,

$$\underset{\text{Diazobenzene.}}{C^6H^4N^2} + H^2O = \underset{\text{Phenol.}}{C^6H^6O} + N^2.$$

This method succeeds not only in the aromatic series strictly so called, but also in the neighbouring series, as those of diphenyl and of naphthalene: thus diamidodiphenyl or benzidine (iv. 411), treated with nitrous acid, yields diazobenzidine or tetrazo-diphenyl:

$$\underset{\text{Benzidine}}{C^{12}H^{12}N^2} + 2NO^2H = \underset{\text{Diazo-benzidine}}{C^{12}H^8N^4} + 4H^2O;$$

and diazobenzidine boiled with water is converted into a diatomic phenol, $C^{12}H^{10}O^2$, with evolution of nitrogen:

$$C^{12}H^8N^4 + 2H^2O = C^{12}H^{10}O^2 + 2N^2$$

(Griess, *Phil. Trans.* 1864, pt. iii. p. 740).

β. By treating an aromatic hydrocarbon with sulphuric acid, whereby a sulpho-acid is produced, which when fused with potash yields the potassium-salt of the corresponding phenol; and by dissolving the salt in water and precipitating with an acid, the phenol is obtained in the free state: thus

$$\underset{\text{Benzene.}}{C^6H^6} + H^2SO^4 = H^2O + \underset{\text{Sulphobenzolic acid.}}{C^6H^6SO^3}$$

$$\underset{\text{Sulphobenzolic acid.}}{C^6H^6SO^3} + 3KOH = \underset{\text{Potassium sulphite.}}{K^2SO^3} + 2H^2O + \underset{\text{Potassium phenate.}}{C^6H^5OK}$$

$$\underset{\text{Potassium phenate.}}{C^6H^5OK} + HCl = KCl + \underset{\text{Phenol.}}{C^6H^5OH}$$

(Wurtz, *Bull. Soc. Chim.* [2] viii. 197; Kekulé, *ibid.* p. 198; Dusart, *ibid.* p. 200).

The phenols are also formed by the destructive distillation of organic bodies, as phenol, C^6H^6O, from salicylic acid, $C^7H^6O^3$. Some of them exist ready-formed in plants, as thymol in oil of thyme, or are produced by the decomposition of certain proximate principles of plants, as pyrogallol from gallic acid and orcin from erythrin:

$$\underset{\text{Gallic acid.}}{C^7H^6O^5} = CO^2 + \underset{\text{Pyrogallol.}}{C^6H^6O^3}$$

$$\underset{\text{Erythrin.}}{C^{20}H^{22}O^{10}} + 2H^2O = \underset{\text{Erythrite.}}{C^4H^{10}O^4} + 2CO^2 + \underset{\text{Orcin.}}{2C^7H^8O^2}$$

(See also p. 202.) Ordinary phenol has been found by Berthelot among the products formed by passing the vapour of alcohol through a red-hot tube.

III. The modes of formation of the aromatic bases have been already mentioned (p. 203).

IV. Of Aromatic Acids: 1. *Monatomic.*—These acids are obtained by several processes similar to those which yield the fatty acids, viz.: *a.* By oxidation of the corresponding alcohols or aldehydes.—*b.* By treating an aromatic hydrocarbon with carbonyl chloride, and decomposing the resulting acid chloride with water (Harnitz-Harnitzky; see p. 39).—*c.* By the action of nascent hydrogen on less hydrogenated acids, as when cinnamic acid, $C^9H^8O^2$, is converted into alphaxylic acid, $C^9H^{10}O^2$ (Erlenmeyer's homotoluic acid, *Jahresb.* 1862, p. 365; 1863, p. 352; Schmitt's cumoylic acid, *ibid.*; Swart's hydrocinnamic acid, *Ann. Ch. Pharm.* cxxxvii. 229), by the action of sodium amalgam (Erlenmeyer; Schmitt), or of hydriodic acid (Popoff, *Bull. Soc. Chim.* [2] iv. 375).—*d.* By heating the hydrocyanic ethers of the aromatic alcohols with alcoholic potash, whereby ammonia is evolved and the potassium salt of an aromatic acid is produced, containing one atom of carbon more than the alcohol-radicle of the cyanide; the acids thus produced are *α*-toluic acid and its homologues: e.g.,

$$\underset{\text{Benzyl cyanide.}}{C^6H^5.CH^2N} + HKO + H^2O = NH^3 + \underset{\text{Potassium } \alpha\text{-toluate.}}{C^6H^5.CH^2CO^2K}$$

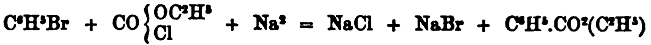
The following methods of formation are peculiar to the aromatic series:

e. Several acids of this series are obtained by oxidation of the hydrocarbons. In this manner toluic acid is produced from cymene, $C^{10}H^{14}$, benzoic acid from cumene, C^9H^{12}, &c.—*f.* By passing a current of carbon dioxide into a brominated aromatic hydrocarbon in which sodium is dissolved. This process yields isomeric products accordingly as the bromine has taken the place of hydrogen in the principal or in one of the lateral chains (Kekulé): thus, for example,

$$\underset{\text{Bromotoluene.}}{C^6H^4Br.CH^3} + Na^2 + CO^2 = NaBr + \underset{\text{Toluate.}}{C^6H^4\left\{\begin{matrix}CH^3\\CO^2Na\end{matrix}\right.}$$

$$\underset{\text{Benzyl bromide.}}{C^6H^5.CH^2Br} + Na^2 + CO^2 = NaBr + \underset{\text{α-toluate.}}{C^6H^5.CH^2CO^2Na}$$

g. As ethers, by treating the monobrominated derivatives of the aromatic hydrocarbons with a chlorocarbonic ether and sodium-amalgam: e.g.,



$$\underset{\text{Bromo-benzene.}}{C^6H^5Br} + \underset{\text{Ethyl chloro-carbonate.}}{CO\left\{\begin{matrix}OC^2H^5\\ Cl\end{matrix}\right.} + Na^2 = NaCl + NaBr + \underset{\text{Ethyl benzoate.}}{C^6H^5.CO^2(C^2H^5)}$$

Bromotoluene treated in like manner yields ethyl toluate (Wurtz, *Compt. rend.* lxviii. 1298).

h. Hofmann (*Proc. Roy. Soc.* xvi. 484) describes a method of obtaining the monatomic aromatic acids from the monamines containing one atom of carbon less. Aniline distilled with one molecule of oxalic acid yields phenyl-formamide:

$$\underset{\text{Aniline.}}{C^6H^5.H^2.N} + \underset{\text{Oxalic acid.}}{C^2O^2.H^2O^2} = \underset{\text{Phenyl-formamide.}}{CHO.C^6H^5.H.N} + H^2O + CO^2,$$

together with a number of secondary products resulting from the decomposition of the formamide, and among them benzonitrile or phenyl cyanide:

$$CHO.C^6H^5.H.N = C^7H^5N + H^2O,$$

the quantity of which may be increased by distilling the product with hydrochloric acid. The benzonitrile, distilled with potash, easily yields benzoic acid. In like manner, toluidine distilled with oxalic acid yields tolyl-formamide, the decomposition of which furnishes toluonitrile, C^8H^7N, and this by distillation with potash yields toluic acid, $C^8H^8O^2$.

i. These acids may also be obtained from the phenols. Potassium phenylsulphate treated with potassium cyanide yields phenyl cyanide or benzonitrile, from which benzoic acid is produced in the manner just mentioned. Similarly toluic acid may be formed from cresyl-sulphuric acid.

k. Several monatomic aromatic acids exist as natural products, or are formed by oxidation of natural aldehydes; thus benzoic acid exists ready formed in gum benzoin, and is produced by oxidation of bitter almond oil.

2. *Diatomic and Monobasic.*—*α.* All the known acids of this group which contain a phenic hydroxyl (except phloretic acid, for which the method has not been tried) are produced by the simultaneous action of sodium and carbon dioxide on the phenols (Kolbe a. Lautemann, *Ann. Ch. Pharm.* cxv. 205): e.g.,

$$\underset{\text{Thymol.}}{2C^{10}H^{14}O} + Na^2 + 2CO^2 = \underset{\text{Sodium thymotate.}}{2C^{11}H^{13}NaO^3} + H^2.$$

Phloretic acid is produced by decomposition of phloretin, which is itself a product of the decomposition of phlorizin.

β. These acids are also produced by the action of nitrous acid on solutions of the mono-amidated acids of the same series in boiling nitric acid:

$$\underset{\text{Amidobenzoic acid.}}{C^7H^5(NH^2)O^2} + NHO^2 = H^2O + N^2 + \underset{\text{Oxybenzoic acid.}}{C^7H^5(OH)O^2}$$

It is better, however, to direct the nitrous acid vapour into a cooled solution of the amidated acid in nitric acid. A diazo-acid is then formed, and this, when boiled with water, gives off nitrogen, and yields the diatomic acid sought:

$$\underset{\text{Amidobenzoic.}}{C^7H^5(NH^2)O^2} + NHO^2 = 2H^2O + \underset{\text{Diazobenzoic.}}{C^7H^4N^2O^2}$$

$$\underset{\text{Diazobenzoic.}}{C^7H^4N^2O^2} + H^2O = N^2 + \underset{\text{Oxybenzoic.}}{C^7H^6O^3}$$

γ. An acid isomeric with oxybenzoic acid, viz. salicylic acid, is produced by oxidation of saligenin, which is a glycophenol (p. 202). The homologues of salicylic acid have not been obtained, because we are as yet unacquainted with any homologue of saligenin, unless it be arbutin (p. 191).

ε. The acids of this group may be formed by the oxidation of certain hydrocarbons, as paraoxybenzoic acid from toluene, or by further oxidation of certain oxygenated products, as anisic (methyl-paraoxybenzoic) acid by oxidation of anise oil (Saytzeff, *Ann. Ch. Pharm.* cxxxvii. 129; Ladenburg, *Bull. Soc. Chim.* [2] v. 257).

Only one diatomic and monabasic acid is known containing an alcoholic and an acid hydroxyl, viz. formobenzoic or mandelic acid, $C^8H^8O^3 = C^6H^5.CHOH.COOH$, which is produced by the simultaneous action of hydrochloric and hydrocyanic acids on oil of bitter almonds dissolved in water. This reaction, however, according to Louguinine and Naquet, does not take place with cuminic aldehyde, on account of its almost total insolubility in water; it is moreover the same as that by which acetic aldehyde in the fatty series is converted into lactic acid.

3. *Of Monobasic acids whose atomicity is greater than three.*—Oxysalicylic and gallic acids have been obtained by processes similar to those employed in the fatty series, viz. by treating monobromo- and dibromo-salicylic acids with silver oxide and water (Lautemann, *Ann. Ch. Pharm.* cxx. 300).

4. *Polybasic.*—There is a series of polybasic aromatic acids intermediate in composition and basicity between benzoic acid (monobasic) and mellitic acid (sexbasic). The pentabasic acid has not yet been obtained; of the bi-, tri-, and quadribasic acids each admits of three modifications, depending upon the relative positions of the groups CO^2H:

	Ortho.	Meta.	Para.
$C^6(CO^2H)^6$	Mellitic		
$C^6H(CO^2H)^5$	Unknown		
$C^6H^2(CO^2H)^4$	Isopyromellitic	Unknown	Pyromellitic acid
$C^6H^3(CO^2H)^3$	Hemimellitic	Trimellitic	Trimesic
$C^6H^4(CO^2H)^2$	Phthalic	Isophthalic	Terephthalic
$C^6H^5(CO^2H)$	Benzoic		

The sexbasic acid, mellitic acid, has not been formed synthetically, and is known only as a natural product obtained from honeystone; the bi-, tri-, and quadribasic acids are formed from it by a regular series of transformations. Thus mellitic acid treated with sodium-amalgam takes up 6 at. hydrogen, yielding hydromellitic acid, $C^6H^6(CO^2H)^6$, which when heated with strong sulphuric acid gives up the 6 at. H and 2 mols. CO^2, and is converted into isopyromellitic acid. This acid treated with sodium-amalgam yields hydro-isopyromellitic acid, $C^6H^4(CO^2H)^4$, which when treated with sulphuric acid is converted by loss of H^4 and CO^2 into hemimellitic acid, $C^6H^3(CO^2H)^3$; and this latter might by a repetition of these operations be converted into bibasic phthalic acid. For further details, see MELLITIC ACID. The bibasic acids, isophthalic and terephthalic, are produced by oxidation of aromatic hydrocarbons containing two lateral chains—isophthalic acid from isoxylene, $C^6H^4(CH^3)^2$; and terephthalic acid from methyl-toluene, amyl-toluene, and diethyl-benzene. Phthalic acid is produced in like manner by oxidation of naphthalene (p. 212).

Azo- and *Diazo-compounds of the Aromatic Series.*

1. *Diazo-compounds.*—The amidated acids and bases of the aromatic series, though similar in composition to those of the fatty series, differ remarkably from them in many of their properties, and especially in their behaviour with nitrous acid. The amidated acids and bases of the fatty series, when treated with nitrous acid, give off water and nitrogen, and reproduce the acid or alcohol whose radicle they contain; thus:

$$\underset{\text{Ethylamine.}}{C^2H^5(H^2N)} + NO^2H = \underset{\text{Ethyl alcohol.}}{C^2H^5(OH)} + H^2O + N^2.$$

Now the amidated bases of the aromatic series are sometimes decomposed by nitrous acid in the same way, aniline for example being converted into phenol, with elimination of nitrogen (iv. 423), but more frequently intermediate products are formed, containing not only the nitrogen of the aromatic base or acid, but also that of the nitrous acid, so that no evolution of nitrogen takes place. The final result is the substitution of N for H^3 in one or in two molecules of the amidated base. Thus aniline or amidobenzene, C^6H^7N, yields by the first of these modes of transformation, diazobenzene or azophenylamine, $C^6H^4N^2$ or $C^6(H^4N''')N$, and by the second, diazo-amidobenzene or azodiphenyldiamine, $C^{12}H^{11}N^3$ or $C^{12}(H^{11}N''')N$.

The compounds of diazobenzene treated with various reagents give rise to a number of remarkable products discovered by Griess, and described in vol. iv. pp. 430-434.

The bases derived from the nitroderivatives of the higher hydrocarbons of the aromatic series give rise to similar but less known products when treated with nitrous acid; but no such products are formed from the amines of the fatty series or from benzylamine, which, as already observed, is analogous in constitution to the latter.

The amidated acids of the aromatic series react with nitrous acid in the same manner as the bases, exchanging N for H^3 in two molecules or in a single molecule, and giving rise to unstable compounds, capable, under the influence of various reagents, of forming chlorinated, brominated, or iodated derivatives of the primitive acid, or an acid more highly oxygenated than that primitive acid. Thus, amidobenzoic or oxybenzamic acid, $C^7H^5(NH^2)O^2$, treated with nitrous acid, yields diazo-amidobenzoic acid, $C^{14}H^{11}N^3O^4 = \begin{cases} C^7H^4N^2O^2 \\ C^7H^7NO^2 \end{cases}$. This latter treated with haloïd acids, yields a hydrochloride, hydrobromide, or hydriodide of amidobenzoic acid, together with chloro-, bromo-, or iodo-benzoic acid. Diazo-amidobenzoic acid treated with alkalis fixes an alkaline molecule, gives off nitrogen and ammonia, and produces a salt of oxybenzoic acid:

$$C^{14}H^{11}N^3O^4 + 2KHO = 2C^7H^5KO^3 + N^2 + NH^3.$$

Oxybenzoic acid is also produced, though in smaller quantity, by the direct action of nitrous acid on amidobenzoic acid. (See OXYBENZAMIC, OXYCUMINAMIC, OXYTOLUAMIC ACIDS, iv. 290, 297, 322.)

When these amidated acids are treated with sodium-amalgam and water, in a cooled vessel, ammonia is given off, and the group NH^2 is replaced by H. In this manner bromamidobenzoic, anthranilic, and amidobenzoic acids have been converted into benzoic acid (Hübner a. Petermann, *Zeitschr. f. Chem.* [2] iv. 548).

2. *Monazo-* or simply *Azo-compounds.*—These bodies are derived from the aromatic hydrocarbons by substitution of N for H in one molecule, or rather of N^2 for H^2 in two molecules of the hydrocarbon.

Mitscherlich in 1834 obtained azobenzene, C^6H^5N or $C^{12}H^{10}N^2$ (i. 478), by treating nitrobenzene with alcoholic potash and subjecting the product to distillation. Zinin in 1845 showed that the first product of this reaction is azoxybenzene, $C^{12}H^{10}N^2O$, which, as well as azobenzene, is converted by reducing agents into the basic compound benzidine, $C^{12}H^{12}N^2$. Hofmann in 1863 (*Proc. Roy. Soc.* xii. 576) showed, however, that the direct product of this reduction is not benzidine, but the isomeric compound hydrazobenzene, capable of passing into benzidine by molecular transformation.

The following formulæ show that the azo-derivatives of benzene are intermediate in composition between nitrobenzene and aniline. In their successive formation, oxygen is first removed, and then hydrogen is added, the product of complete reduction being aniline:

	Empirical formulæ.		Molecular formulæ.
Nitrobenzene	$C^6H^5NO_2$	=	$C^6H^5NO^2$
Azoxybenzene	$C^6H^5NO_{\frac{1}{2}}$	=	$C^{12}H^{10}N^2O$
Azobenzene	C^6H^5N	=	$C^{12}H^{10}N^2$
Hydrazobenzene (and Benzidine)	C^6H^6N	=	$C^{12}H^{12}N^2$
Aniline	C^6H^7N	=	C^6H^7N.

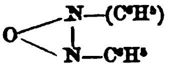
The same bodies can also be produced, as Glaser has shown (*Ann. Ch. Pharm.* cxlii. 364) by successive oxidation, starting from aniline.

Azoxybenzene treated with nitric acid yields a mononitro-derivative, of which there are isomeric modifications (i. 480); with a mixture of strong nitric and sulphuric acids, it yields a trinitrated compound. Azobenzene yields two nitro-derivatives, $C^{12}H^9(NO^2)N^2$ and $C^{12}H^8(NO^2)^2N^2$. The latter treated with ammonium sulphide is reduced to diamido-azobenzene or diphenine, $C^{12}H^8(NH^2)^2N^2$ (ii. 336). The former has not yet, with certainty, been reduced to amido-azobenzene, $C^{12}H^9(NH^2)N^2$; but this compound is obtained, together with amido-azoxybenzene, $C^{12}H^9(NH^2)N^2O$, by reduction of mononitro-azoxybenzene (G. A. Schmidt); also by the action of various oxidising agents upon aniline (Martius a. Griess), and by the action of aniline and its salts on diazo-amidobenzene (Kekulé).

Compounds homologous with azobenzene have recently been obtained from nitrotoluene, nitroxylene, and even from nitrocumene and nitrocymene. For the particular descriptions of these compounds, see the several hydrocarbons.

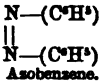
The following theory of the constitution of the azo- and diazo-compounds is given by Kekulé (*Lehrbuch d. org. Chemie,* ii. 689, 715, 741; *Zeitschr. f. Chem.* 1866, pp. 308, 689, 700).

The azo-compounds contain a group of two nitrogen-atoms united to one another by a part of their combining capacities, and therefore capable of acting only with the remainder. In the azo-compounds these two nitrogen-atoms are directly combined with the carbon of a benzene residue; in azobenzene they act as a bivalent group, in azoxybenzene and hydrazobenzene as a quadrivalent group; while on further addition of hydrogen all the combining units of the nitrogen become active, and the molecule splits into two; thus:



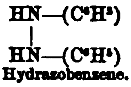
$$O\begin{array}{l}\diagup N-(C^6H^5)\\ \quad\; | \\ \diagdown N-C^6H^5\end{array}$$

Azoxybenzene.



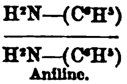
$$\begin{array}{l}N-(C^6H^5)\\ \| \\ N-(C^6H^5)\end{array}$$

Azobenzene.



$$\begin{array}{l}HN-(C^6H^5)\\ \;\,| \\ HN-(C^6H^5)\end{array}$$

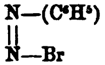
Hydrazobenzene.



$$\begin{array}{l}H^2N-(C^6H^5)\\ \hline H^2N-(C^6H^5)\end{array}$$

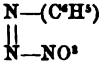
Aniline.

The diazo-compounds likewise contain the bivalent group $(NN)''$, but only one of the nitrogen-atoms is directly combined with the carbon of a benzene residue, while the free affinity of the other is satisfied, either by haloïds or by acid residues, or amidogen, or generally in some way different from the first. From the chemical relations of the diazobenzene-compounds in particular, Kekulé infers that diazobenzene in the free state consists, not of $C^6H^4N^2$, as supposed by Griess, but of the hydrate corresponding to the potash and silver-oxide compounds of diazobenzene (iv. 434); thus:



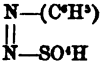
$$\begin{array}{l}N-(C^6H^5)\\ \| \\ N-Br\end{array}$$

Diazobenzene bromide.



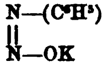
$$\begin{array}{l}N-(C^6H^5)\\ \| \\ N-NO^3\end{array}$$

Diazobenzene nitrate.



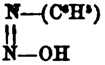
$$\begin{array}{l}N-(C^6H^5)\\ \| \\ N-SO^4H\end{array}$$

Diazobenzene sulphate.



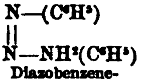
$$\begin{array}{l}N-(C^6H^5)\\ \| \\ N-OK\end{array}$$

Diazobenzene-potash.



$$\begin{array}{l}N-(C^6H^5)\\ \| \\ N-OH\end{array}$$

Diazobenzene hydrate.



$$\begin{array}{l}N-(C^6H^5)\\ \| \\ N-NH^2(C^6H^5)\end{array}$$

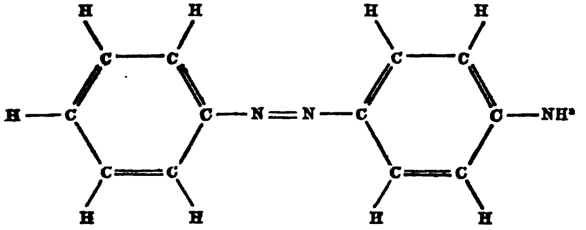
Diazobenzene-amidobenzene.

According to this view, the relation of the azo-compounds to the diazo-compounds is similar to that of the alcoholic oxides, or simple ethers, to the haloïd ethers and oxacid ethers: e.g.,

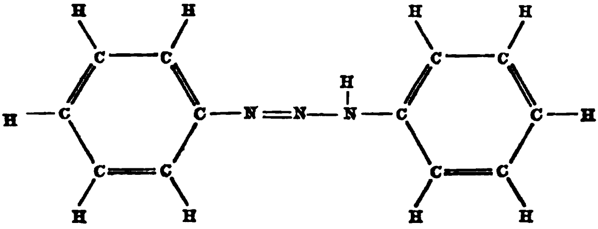
$(C^6H^5)-N\overset{..}{=}N-(C^6H^5)$ Azobenzene. $(C^6H^5)-N\overset{..}{=}N-NO^3$ Diazobenzene nitrate.

$(C^2H^5)-\ddot{O}-(C^2H^5)$ Ethyl oxide. $(C^2H^5)-\ddot{O}-NO^2$ Ethyl nitrate.

The relation between the isomeric compounds amido-azobenzene (amido-diphenylimide) and diazo-amidobenzene may be represented by the following formulæ:



Amido-azobenzene.



Diazo-amidobenzene.

Both these bodies contain the group $(C^6H^5)-N{=}N-$ joined to a residue containing C^6H^6N; but in amido-azobenzene the nitrogen group NN is joined to this residue by an atom of carbon; whereas in diazo-amidobenzene the connection is made through the medium of a third atom of nitrogen. Diazo-amidobenzene is in fact converted into amido-azobenzene by the action of an aniline-salt, the aniline-residue $NH(C^6H^5)$

It is easy to see that these compounds admit of numerous isomeric modifications according to the relative position of the group OH, NH^2, CO^2H, &c., in one or both of the associated benzene residues.

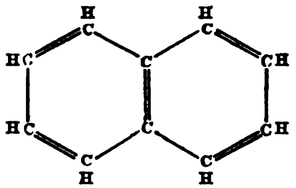
3. **Naphthalene.** $C^{10}H^8$.—This hydrocarbon, in its chemical relations, exhibits a very close analogy to benzene. It forms numerous bromo-, chloro-, and nitro-derivatives; its hydroxide, naphthol, $C^{10}H^7(OH)$, is a true phenol; its mono-nitro-derivative reduced by nascent hydrogen yields a base, $C^{10}H^7(NH^2)$, analogous to aniline, and undergoing transformations similar to those of the latter under the influence of nitrous acid. Moreover, naphthylamine distilled with oxalic acid yields naphthyl-formamide, $C^{11}H^9NO$, the dehydration of which gives rise to the corresponding nitrile, $C^{11}H^7N$; and by distilling this compound with potash, naphthoic acid, $C^{11}H^8O^2$, is obtained, which is related to naphthylamine in the same manner as benzoïc acid to aniline.

The structure of the naphthalene molecule is deduced by Graebe (*Ann. Ch. Pharm.* cxlix. 20) from the following considerations. Naphthalene is converted by oxidation into phthalic or benzene-dicarbonic acid, $C^6H^4(CO^2H)^2$, two of its carbon-atoms being removed as carbon dioxide, while two others remain in the form of carboxyl:

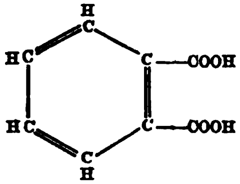
$$C^{10}H^8 + O^9 = C^6H^4(CO^2H)^2 + 2CO^2 + H^2O.$$

Hence naphthalene contains a benzene-residue, C^6H^4, and may be represented by the formula $C^6H^4(C^4H^4)''$. But phthalic acid is likewise produced by oxidation of dichloronaphthoquinone, $C^{10}H^4Cl^2(O^2)''$; consequently, this compound has its two chlorine-atoms and two oxygen-atoms associated with the four carbon-atoms which undergo oxidation, and may be represented by the formula $C^6H^4[C^4Cl^2(O^2)'']''$. By the action of phosphorus pentachloride, the two oxygen-atoms are replaced by two chlorine-atoms, and at the same time one of the four hydrogen-atoms is replaced by chlorine, the result being pentachloronaphthalene, $C^6H^3Cl(C^4Cl^4)$. If now, when this last compound is oxidised, the same four carbon-atoms were attacked as in the case of dichloronaphthoquinone, the result would be monochlorophthalic acid, $C^6H^3Cl(CO^2H)^2$; but Graebe has shown that the actual product of the oxidation of pentachloronaphthalene is tetrachlorophthalic acid, $C^6Cl^4(CO^2H)^2$. In this reaction, therefore, two of the carbon-atoms belonging to the left-hand group in the molecule $C^6H^3Cl(C^4Cl^4)$ are removed as carbon dioxide, while two others yield the two groups CO^2H, and the remaining two, together with the four standing on the right, form the benzene nucleus C^6Cl^4 of tetrachlorophthalic acid.

These transformations show that the molecule of naphthalene is symmetrical, and composed of two benzene-nuclei united in the manner represented by the following figure:



In the oxidation of this molecule to phthalic acid, two of the carbon-atoms from one benzene-nucleus may be supposed to go out as CO^2, while the other two, which are in immediate connection with the second benzene-nucleus, yield the two carboxyl-groups; thus:



The mode of this transformation shows that the two carboxyl-groups in phthalic acid are contiguous, or occupy the position 1, 2; and this, combined with other considerations, leads, as already explained (p. 198), to a determination of the relative positions of the radicles in the ortho-, meta-, and para-compounds of the benzene group.

The relations between naphthalene and its above-mentioned derivatives may also be represented by the following condensed formulæ:

$C^4H^4(C^2)C^4H^4$
Naphthalene.

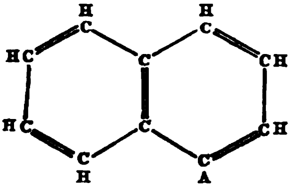
$C^4H^4(C^2)C^4Cl^2(O^2)''$
Dichloronaphthoquinone.

$C^4H^3Cl(C^2)C^4Cl^4$
Pentachloronaphthalene.

$C^4H^4(C^2)(CO^2H)^2$
Phthalic acid.

$C^4Cl^4(C^2)(CO^2H)^2$
Tetrachlorophthalic acid.

The structural formula of naphthalene above given leads to the inference that there must be two series of isomeric compounds formed by the replacement of a single atom of hydrogen in naphthalene by chlorine, bromine, hydroxyl, &c., inasmuch as the hydrogen-atoms adjacent to the two carbon-atoms which are common to both the benzene-nuclei, may be supposed to differ in their functions from the other four. In this manner two isomeric compounds may be formed; thus:



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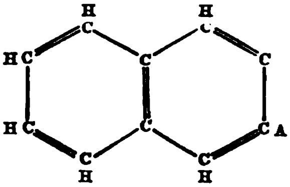
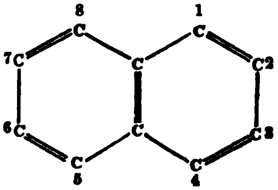


The two naphthalene monosulpho-acids discovered by Faraday (v. 561) afford an instance of this isomerism. (See NAPHTHALENE-COMPOUNDS.)

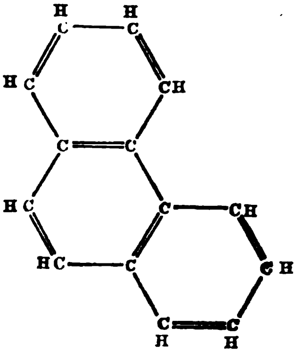
More complicated cases of isomerism arise when two hydrogen-atoms belonging to the same or to different benzene-residues in the naphthalene molecule undergo replacement. The existence of such isomerides may in general be detected by oxidising them, and examining the phthalic acid thereby produced. There will probably be four cases of isomerism in which both the replacing radicles enter into the same benzene nucleus, and eight in which they enter both nuclei. If the hydrogen-atoms in naphthalene be numbered from 1 to 8, thus:



the twelve cases of isomerism will be as follows:

1, 2   1, 3   1, 4   2, 3
1, 5   1, 6   1, 7   1, 8   2, 5   2, 6   2, 7   2, 8.

4. **Anthracene** and **Alizarin.** The synthesis of anthracene, $C^{14}H^{10}$, from benzyl-chloride, $C^6H^5.CH^2Cl$ (p. 176), might lead to the conclusion that it is made up of two benzene-residues, C^6H^5, connected by two atoms of carbon, or, in other words, that it is a phenylated-acetylene, $C^6H^5—C\equiv C—C^6H^5$; but the formation of phthalic acid, $C^6H^4(CO^2H)^2$, by oxidation of a derivative of anthracene, viz. alizarin, $C^{14}H^4(OH)^2(O^2)''$, is not compatible with this formula. Moreover, as benzene, C^6H^6, naphthalene, $C^{10}H^8$, and anthracene, $C^{14}H^{10}$, form a series whose common difference is C^4H^2, and as naphthalene is made up of two benzene-rings, it is very probable that anthracene is made up of three such rings united together thus:



or, in more condensed form:

$$\begin{array}{lcl} C^6H^4 & \text{——} & CH \\ | & & \| \\ C^6H^4 & \text{——} & CH \end{array} \qquad \text{or} \qquad C^{14}\left\{\begin{array}{l} H^4 \\ \overline{H^2} \\ \overline{H^4}. \end{array}\right.$$

This structural formula affords an easy explanation of the production of anthracene from two molecules of benzyl chloride, $\left\{\begin{array}{l} C^6H^4(H)\text{—}CH(HCl) \\ C^6H^4(H)\text{—}CH(HCl) \end{array}\right\}$. Each of the two benzene-residues, C^6H^5, loses an atom of hydrogen (indicated by the brackets), and the two residues, C^6H^4, then unite together. At the same time, each of the lateral chains, CHHCl, loses a molecule of hydrochloric acid, and the two carbon-atoms then attach themselves to each other by two units of affinity.

The formation of phthalic acid by oxidation of alizarin, $C^{14}H^6(OH)^2(O^2)''$, shows that in this compound the two quinonic oxygen-atoms and the two hydroxyls are contained in the middle and one of the external benzene-rings, so that the formula of alizarin is one of the two following:

$$C^{14}\left\{\begin{array}{l} H^4 \\ \overline{(O^2)''} \\ \overline{H^2(OH)^2} \end{array}\right. \quad (1) \quad \text{or} \quad C^{14}\left\{\begin{array}{l} H^4 \\ \overline{(OH)^2} \\ \overline{H^2(O^2)''} \end{array}\right. \quad (2)$$

According to either of these formulæ, the formation of phthalic acid from alizarin is explained by supposing that the benzene nuclei containing the oxygen are oxidised, and converted into the two carboxyls, which remain combined with the third nucleus, and into oxalic or carbonic acid which separates. If all the oxygen-atoms of alizarin were contained in one of the external nuclei, the product of the oxidation would be a naphthalene-dicarbonic acid, $C^{14}H^6(CO^2H)^2$; and if the quinonic oxygen-atoms and the hydroxyls were distributed between the two exterior nuclei, the oxidised product would be a substituted phthalic acid or a benzene-tetracarbonic acid.

Of the two formulæ of alizarin above given (1) appears to be the more probable, for the following reasons:—Benzene cannot be directly oxidised to quinone, and naphthalene is with difficulty oxidised to naphthoquinone; but anthracene is very easily oxidised to anthraquinone. This seems to show that the formation of a quinone is facilitated by accumulation of carbon-atoms; but in anthracene the hydrogen-atoms belonging to the middle ring are more surrounded by carbon than the rest, and will therefore be the most readily oxidised. This view is further corroborated by the great stability of anthraquinone; if the two oxygen-atoms in this body were contained in one of the external nuclei, it would probably oxidise more easily, yielding a naphthalene-dicarbonic acid. Finally, the formation of anthraquinone from dibromanthracene by the action of oxidising agents which do not convert dibromobenzene or dibromonaphthalene into the corresponding quinones, renders it probable that the two bromine-atoms in this compound have replaced the hydrogen-atoms belonging to the middle ring. On these grounds the brominated and quinonic derivatives of anthracene may be formulated as follows:

$$C^{14}\left\{\begin{array}{l} H^4 \\ \overline{Br^2}, \\ H^4 \end{array}\right. \text{Dibromanthracene.} \qquad C^{14}\left\{\begin{array}{l} H^4 \\ \overline{Br^2} \\ H^4.\overline{Br^4} \end{array}\right. \text{, Dibromanthracene-tetrabromide.}$$

$$C^{14}\left\{\begin{array}{l}H^4\\ \overline{Br^2}\\ \overline{H^2Br^2}\end{array}\right., \text{ Tetrabromanthracene.} \qquad C^{14}\left\{\begin{array}{l}H^4\\ (\bar{O}^2)''\\ \overline{H^4}\end{array}\right., \text{ Anthraquinone.}$$

$$C^{14}\left\{\begin{array}{l}H^4\\ (\bar{O}^2)''\\ \overline{H^2(OH)^2}\end{array}\right., \text{ Alizarin.}$$

(Graebe a. Liebermann, *Zeitschr. f. Chem.* [2] iv. 279; vi. 262).

ARSENIC. According to Ludwig (*Arch. Pharm.* [2] xcvii. 23), sublimed arsenic may be obtained with a perfectly bright surface by heating it in a test-tube with a small quantity of iodine, which converts the thin crust of suboxide usually present into arsenious oxy-iodide, $2AsI^3.As^2O^3$, the vapour of the iodide protecting the residual arsenic from oxidation. It then resembles freshly granulated zinc, and has a density of 5·395.

Under ordinary circumstances metallic arsenic sublimes at 180° without previous fusion; but when heated to low redness under pressure it melts into globules (Landolt, *Jahresb.* 1859, p. 182). According to Hittorf (*ibid.* 1865, p. 133), it sublimes without the slightest sign of fusion when heated in a vacuous glass tube.

According to Bettendorff (*Ann. Ch. Pharm.* cxliv. 110), when arsenic is sublimed in a tube of hard glass through which a stream of hydrogen is passing, it condenses near the heated part of the tube in hexagonal crystals, and at some distance beyond in an amorphous black glassy crust, while the farthest portion of the tube becomes coated with a powder which appears yellow at first, but quickly turns grey. The condition essential to the deposition of the amorphous vitreous arsenic is the cooling of the vapour to 210°–220°. This amorphous arsenic is most easily obtained by sublimation in an exhausted tube or in a combustion-tube bent U-shape at one end, and dipping at this end into an oil-bath heated to 220°, while the arsenic lying just above the bend is volatilised in the stream of hydrogen; the U-tube then becomes lined with a specular coating of amorphous arsenic, which may be loosened by a few blows. Its sp. gr. is 4·710 to 4·716 (4·69 according to Hittorf, *Jahresb.* 1865, p. 130), therefore much below that of the crystalline variety. When heated to 360° it is converted, with evolution of heat, into crystalline arsenic, and if the heat be quickly applied, the change is accompanied by a hissing noise and formation of vapour. It is somewhat less oxidisable than crystalline arsenic, changes but slowly in damp air, and is attacked with difficulty even by dilute nitric acid. The mirror of arsenic obtained in Marsh's apparatus appears to belong to the same modification. The pulverulent arsenic above mentioned exhibits under the microscope the form of spherules strung together like pearls. Its sp. gr. is 4·710 at 14° (4·72 according to Hittorf). At 360° it passes, with great rise of temperature, into the crystalline modification, but it is more readily oxidisable than the amorphous vitreous variety. The yellow powder deposited at the beginning of the process is perhaps a third modification, but it was not obtained pure. Pure crystalline arsenic, after repeated sublimation in a stream of hydrogen, has, according to Bettendorf, a sp. gr. of 5·726–5·728 at 14°.

The specific heat of crystallised arsenic repeatedly sublimed in a stream of hydrogen is 0·0830; that of amorphous arsenic prepared from the crystallised variety by sublimation in a vacuous tube at a low temperature is 0·0758 (Bettendorff a. Wüllner, *Zeitschr. f. Chem.* [2] iv. 560).

An aqueous solution of arsenious fluoride yields by electrolysis a scaly precipitate of metallic arsenic exhibiting faint thermic properties analogous to those of amorphous antimony (Gore, *Chem. Soc. J.* [2] i. 365).

According to Le Roux (*Compt. rend.* li. 171), the vapour of arsenic has a lemon-yellow colour.

Metallic arsenic heated to 200° in a sealed tube with solution of sulphurous acid, yields arsenious oxide, sulphuric acid, and free sulphur, but no sulphide of arsenic (Gittner, *Jahresb.* 1864, p. 143).

Detection of Arsenic. *a. Reinsch's test.*—A solution containing arsenic acid or an alkaline arsenate mixed with sulphuric acid does not produce any deposit on metallic copper, even after long boiling, unless the quantity of arsenic present is somewhat considerable; the deposition may however be ensured by adding sulphurous acid or a sulphite, whereby the arsenic acid is reduced to arsenious acid (G. Werther, *J. pr. Chem.* lxxxii. 286; *Jahresb.* 1861, p. 851). The grey deposit formed on copper in a solution of arsenious acid is not pure metallic arsenic, but an arsenide of copper, Cu^8As^2 (containing 32 p. c. arsenic). When ignited for some time in a stream of hydrogen, it gives off part of its arsenic and is reduced to Cu^3As^2 (G. Lippert, *J. pr. Chem.* lxxxi. 168; *Jahresb.* 1860, p. 170).

β. Marsh's test.—E. Davy (*Jahresb.* 1858, p. 609) recommends the use of *platinum* in the form of thick plate (not thin foil) instead of porcelain or glass for receiving the spots formed by ignited arsenetted hydrogen. The spots adhere closely to the metal, and disappear with garlic odour when gently heated. Antimony spots received on platinum do not disappear when heated over a spirit-lamp.

Very small arsenic spots on porcelain or platinum may be recognised by volatilising them and receiving the vapours on the object-glass of a microscope. Spots of pure arsenic or of arseniferous antimony thus treated yield a deposit of octohedral arsenious oxide, whereas spots of pure antimony do not yield any deposit on the object-glass (Hellwig, *Das Microscop in der Toxicologie*).

According to Blondlot (*Jahresb.* 1863, p. 681), the presence of nitric acid in the liquid, even in small quantity, prevents the formation of gaseous hydride of arsenic, the solid hydride, As^4H^2, being then deposited in brown flocks upon the zinc.

Roussin (*Jahresb.* 1866, p. 801) recommends the use of *magnesium* instead of zinc in Marsh's apparatus. Arsenic and antimony are thereby evolved as hydrogen-compounds, while any non-volatile metals that may be present are thrown down in the form of a metallic precipitate, which may be collected on a filter and further examined. If the magnesium contains silicon, siliciuretted hydrogen will be evolved; but the spots which this gas produces on porcelain are easily distinguished from arsenic and antimony spots by their insolubility in nitric acid, nitromuriatic acid, and sodium hypochlorite.

Arsenetted hydrogen is easily converted into an iodide of arsenic by passing it over gently heated iodine. If a small quantity of iodine be introduced into the tube of Marsh's apparatus and gently warmed, so as to form on cooling a deposit on the part of the tube on which the arsenic mirror is usually produced, then, if a stream of hydrogen containing arsenic be passed through the tube while still lukewarm, iodide of arsenic will be formed, as a yellow deposit consisting of microscopic laminæ, very much like iodoform, and the iodine will disappear completely. Antimonious hydride acts upon iodine in a similar manner, but less quickly, the iodine uniting into a deep-coloured ring, which gradually becomes brown towards the drawn-out end of the tube, and orange-yellow towards the apparatus. This coloured ring does not spread itself further, and the iodine does not disappear completely. The two iodides may also be readily distinguished by their behaviour when heated. The yellow iodide of arsenic then partly sublimes unaltered, and is partially converted, with liberation of iodine, into a red iodide, indicating the previous formation of arsenic iodide, AsI^3. The iodide of antimony, on the other hand, gives off red vapours and leaves reduced antimony (C. Hasson, *Compt. rend.* lxvii. 56).

γ. Zenger's process (*Zeitschr. Chem. Pharm.* 1862, p. 38; *Jahresb.* 1862, p. 595).—This method consists in the production of a specular deposit of arsenic by reducing magnesium arsenate with *sodium oxalate* in a sealed tube filled with carbon dioxide. The substance under examination is repeatedly distilled with a mixture of equal volumes of strong hydrochloric acid and water; the arsenic is precipitated from the distillate as sulphide; the precipitated arsenious sulphide is evaporated down with nitric acid free from chlorine; and the residue is fused with pure sodium nitrate. From the sodium arsenate thus obtained the arsenic is precipitated as ammonio-magnesium arsenate; the precipitate after drying at 100° is mixed with a little anhydrous sodium carbonate to make it more manageable, and then ignited to expel the ammonia; and the magnesium arsenate thus produced is mixed with 10 times its weight of dry sodium oxalate, and a little charcoal powder to colour the mixture. On the other hand, 20 parts of dry sodium oxalate are introduced into a tube of thin, easily fusible glass, 3 millimetres in diameter and sealed at one end; the blackened mixture, weighing about 11 pts., is introduced above the oxalate; and the tube, after the empty part has been carefully cleaned, is drawn out to a fine neck. The tube is next heated, first at the bottom to evolve carbon monoxide and expel the air, the heat being gradually extended up to the coloured mixture; after which the tube is sealed, and heat is applied to the arseniferous mixture. The smallest quantity of arsenic is thereby deposited close above the mixture, in a beautiful, compact, metallic ring. The sealing of the tube prevents loss of arsenic.

δ. Bettendorff's process (*Zeitschr. f. Chem.* [2] v. 492).—When a solution of *stannous chloride* in fuming hydrochloric acid is added to a solution of arsenious or arsenic oxide in the same acid, a brown precipitate is formed, which, after proper washing and drying, consists of metallic arsenic mixed with a small quantity of stannic oxide. In an aqueous solution of arsenious or arsenic acid, stannous chloride produces no precipitate; but on adding strong hydrochloric acid till the liquid fumes slightly, precipitation takes place. Arseniferous hydrochloric acid of sp. gr. 1·182 to 1·135 gives an immediate precipitate; the same diluted to sp. gr. 1·115 gives imperfect precipitation after some time; and in a similar solution of sp. gr. 1·100 no precipitation takes place. From this it may be inferred that the reaction occurs only between stannous chloride and arsenious chloride; further, that in a solution of arsenious acid in hydrochloric acid of sp. gr. 1·115 part of the arsenic is present as chloride, but that hydrochloric acid of sp. gr. 1·100 dissolves arsenious acid as such, without converting it into chloride. The reaction above described is extremely delicate and capable of detecting 1 pt. of arsenic in a million parts of solution. On antimony-compounds stannous chloride exerts no reducing action, even after prolonged heating: hence the above-described reaction may be used to detect the presence of arsenic in antimony-compounds, the solution being previously saturated with hydrochloric acid gas. Another useful application of the same reaction is to the preparation of hydrochloric acid free from arsenic. 421 grms. of crude hydrochloric acid of sp. gr. 1·164 were mixed with a fuming solution of stannous chloride, the precipitate separated by filtration after 24 hours, and the hydrochloric acid distilled, the receiver being changed after the first tenth had passed over, and the remaining liquid distilled nearly to dryness. The acid thus obtained gave not the slightest indications of arsenic, either by Marsh's test or by precipitation with hydrogen sulphide.

In testing for arsenic acid with silver nitrate, the delicacy of the reaction is impaired by the solubility of silver arsenate, not only in free nitric acid and free ammonia, but also in ammonium nitrate. According to C. Avery (*Sill. Am. J.* [2] xlvii. 25), the reaction is greatly facilitated by adding to the solution of arsenic acid in nitric acid a few drops of a strong solution of an alkaline acetate, and then a drop or two of ammoniacal silver nitrate. Another very good mode of testing is to drop the nitric acid solution of arsenic acid on recently prepared silver carbonate, the red silver arsenate then showing itself very conspicuously on the white ground.

Metallic arsenic and arsenious acid are easily oxidised by a mixture of potassium chlorate and nitric acid to arsenic acid, which may then be easily estimated as ammonio-magnesian arsenate (A. H. Pearson, *Sill. Am. J.* [2] xlviii. 190).

Compounds of Arsenic.

Bromide. $AsBr^3$.—Prepared by adding pulverised arsenic to a mixture of 1 pt. bromine and 2 pts. carbon bisulphide, agitating till the liquid becomes colourless, then adding more bromine, then again arsenic, and so on till the solution is saturated, i.e. till it is no longer decolorised on further addition of arsenic. Crystallises in deliquescent colourless prisms, having a strong arsenical odour, volatilising undecomposed, and yielding a crystalline sublimate. Decomposed by water with separation of arsenious oxide. In contact with sodium hyposulphite, it first forms arsenious oxybromide, and then becomes covered with arsenious sulphide. It unites with the bromides of the alkali-metals, forming rather unstable crystallisable compounds (Nicklès, *J. Pharm.* [3] xli. 142). Its specific gravity at mean temperatures is 3·66 (Bödeker, *Jahresb.* 1860, p. 17).

Chloride. $AsCl^3$.—This compound is formed, together with arsenious arsenate, $2As^2O^3.As^2O^5$, when dry chlorine is passed over pulverised and gently heated arsenious oxide:

$$11As^2O^3 + 6Cl^2 = 4AsCl^3 + 3(2As^2O^3.As^2O^5).$$

(Bloxam, *Chem. Soc. J.* [5] iii. 62). Also by the action of 2 at. arsenic on 3 at. sulphur dichloride, sulphur being separated at the same time, partly in opaque prisms, partly in bulky transparent octohedrons (Chevrier, *Compt. rend.* lxiii. 1003; *Jahresb.* 1866, p. 212):

$$As^2 + 3SCl^2 = 2AsCl^3 + S^3.$$

Arsenious chloride is also produced by distilling a mixture of arsenious sulphide and mercuric chloride (Ludwig, *Jahresb.* 1859, p. 187).

A compound of arsenious chloride with *alcohol*, apparently $AsCl^3.C^2H^6O$, is produced by mixing the chloride with absolute alcohol, and passes over on distillation at 148°; also by passing hydrochloric acid gas into alcohol containing arsenious oxide in suspension, and subjecting the lower of the two resulting liquids to fractional distillation. It is a colourless liquid which fumes in the air; is decomposed by water or by atmospheric moisture into hydrochloric acid, arsenious acid, and alcohol; and absorbs hydrochloric acid gas abundantly and with rise of temperature, giving it up again on distillation. It is partially decomposed by repeated distillation, yielding ethyl chloride, &c. Arsenious chloride appears to form similar compounds with methylic and amylic alcohols (V. de Luynes, *Compt. rend.* l. 831).

A compound of arsenious chloride with *aniline*, $AsCl^3.3C^6H^7N$, formed by direct combination, is described under PHENYL-AMMONIUMS (iv. 474).

Fluorides. The *trifluoride*, AsF^3, is described in vol. i. p. 371. The *pentafluoride* or *arsenic fluoride*, AsF^5, is not known in the free state, but some of its double salts have been prepared by Marignac (*Ann. Ch. Pharm.* cxlv. 237; *Jahresb.* 1867, p. 254).

Potassio-arsenic fluoride, $2(KF.AsF^5).H^2O$, is formed by dissolving potassium arsenate in excess of hydrofluoric acid, and crystallises from the concentrated solution in small well-developed rhombic prisms, exhibiting the combination $P . \frac{1}{3}P . \infty\bar{P}\infty . \infty\breve{P}\infty . \infty\bar{P}2 . \bar{P}\infty . \frac{1}{2}P\infty . \breve{P}\infty . \frac{1}{3}\breve{P}\infty . oP$. The crystals are tabular from predominance of oP or $\infty\bar{P}\infty$, and these faces, as well as the macrodomes, are strongly striated. Angle $P : P$ (macr.) = 84°; $oP : P$ = 104° 20′; $oP : \breve{P}\infty$ = 111° 40′; $oP : \frac{1}{3}\breve{P}\infty$ = 140° 20′. The salt when heated in a tube, melts and gives off water and hydrofluoric acid. Its solution is slowly precipitated by hydrogen sulphide. By repeated evaporation it ultimately yields *potassio-arsenic oxyfluoride*, $KF.AsOF^3 + H^2O$, in acute rhombic plates. The same compound is obtained by dissolving potassium arsenate in an insufficient quantity of hydrofluoric acid. On mixing the solution of either of the preceding salts with excess of potassium fluoride and hydrofluoric acid, evaporating the solution, and leaving it to cool, *dipotassio-arsenic fluoride*, $2KF.AsF^5 + H^2O$, crystallises out in large shining rhombic prisms, permanent in the air, and usually exhibiting the simple combination $\infty P . oP$, sometimes also with the faces $P . \infty\breve{P}\infty . \infty\breve{P}2 . \breve{P}\infty . 2\breve{P}\infty$. Angle $\infty P : \infty P$ = 97°; $\infty\breve{P}2 : \infty\breve{P}2$ (brach.) = 132° 4′; $oP : \breve{P}\infty$ = 147° 10′. By repeated evaporation and redissolution this salt is converted into the double salt $2KF.AsOF^3 + 2KF.AsF^5 + 3H^2O$. The same compound crystallises from a solution of monopotassio-arsenic oxyfluoride mixed with neutral potassium fluoride. It forms shining crystals, exhibiting a very large number of faces, generally also intergrown, and consequently not exactly determinable.

Hydrides. When arsenious hydride, AsH^3, is passed through *sulphuric acid* of sp. gr. 1·26 to 1·843, the acid first turns brown, and if the stream of gas be continued, deposits a brown flocculent precipitate, mixed at a subsequent stage with arsenious sulphide, while hydrogen sulphide is evolved. After the passage of the gas had been continued for an hour, the precipitate was found to contain 95 p. c. arsenic, 4·6 sulphur, 0·29 to 0·32 hydrogen, and at a somewhat later stage of the process 88·4 p. c. arsenic to 9·4 sulphur. Hence it appears probable that the precipitate is a mixture of the solid hydride, metallic arsenic, and arsenious sulphide (Th. Humpert. *J. pr. Chem.* xciv. 392; *Jahresb.* 1865, p. 226).

Arsenious hydride is completely decomposed by *chlorine*, with deposition of metallic arsenic (Soubeiran, *Gmelin's Handbook*, iv.; Wiederhold, *Pogg. Ann.* cxviii. 615; *Jahresb.* 1863, p. 231); in contact with *air*, *nitric acid*, or *nitrogen dioxide*, on the other hand, it deposits a mixture of metallic arsenic with the solid hydride (Wiederhold).

This solid hydride may be obtained nearly pure (mixed only with a little carbon), by treating a granulated alloy of 1 pt. arsenic and 5 pts. zinc[*] with hydrochloric acid, and washing the undissolved brown powder with water. The product amounts to only ⅓ p. c. of the alloy used. From the quantity of hydrogen evolved from it by heat, it appears to have nearly the composition As^2H, or rather As^4H^2.[†] It is a bulky red-brown powder, insoluble in water, alcohol, ether, oil of turpentine, and carbon disulphide. It is resolved at 200° into arsenic and hydrogen, and burns away with a glimmering yellow light when heated in the air. In fuming *nitric acid* it burns with emission of light; in nitric acid of sp. gr. 1·2 it oxidises more slowly; other dilute acids have no action upon it. *Chlorine*, *bromine*, and *iodine* decompose it with incandescence. Aqueous *alkalis* slowly convert it into arsenic acid. Its dust produces inflammation of the mucous membrane of the nose (Wiederhold, *loc. cit.*).

According to Blondlot (*Ann. Ch. Phys.* [3] lxviii. 186), the same solid hydride of arsenic is produced in Marsh's apparatus (instead of the gaseous hydride), if the liquid contains even small quantities of nitric acid; but if the zinc contains small quantities of any other metal (lead or tin), or if organic substances are present, the solid hydride is formed in smaller quantity only or not at all. When the gaseous hydride is passed through a solution of silver nitrate, and the silver is then precipitated by hydrochloric acid, the filtrate acidulated with nitric acid deposits on a plate of zinc easily recognisable flocks of the solid hydride.

Respecting the reaction of arsenious hydride with *iodine*, see p. 216.

Oxides. 1. *Arsenious Oxide.* *Dimorphism.*—This oxide crystallises in regular octohedrons, or in crystals belonging to the rhombic system, the latter being produced for the most part at high, the former at low temperatures. Prismatic arsenious oxide occurs in the mines of St. Domingo in Portugal, forming thin plates, some of which are more than an inch long. The crystals are not perfectly developed, but some of them exhibit hemitropy similar to that of gypsum. They are colourless, semitransparent, nacreous, tough, flexible, and easily split into thin lamellæ. Sp. gr. = 3·85. Hardness = 2·5 (ordinary arsenious oxide gave 2·76 p. c.). The crystals sublime without residue when heated, but cannot be obtained again in the prismatic form, either by sublimation or by crystallisation from solution (F. Claudet, *Chem. Soc. J.* [2] vi. 179). Prismatic arsenious oxide has also been found by Scheurer-Kestner (*Zeitschr. f. Chem.* [2] v. 486) in a furnace used for the roasting of pyrites. F. Ulrich (*Jahresb.* 1858, p. 173) describes crystals of arsenious oxide occurring as a roasting product of the Rammelsberg ores at the Oker works in the Harz, which were externally rhombic ($\infty P \,.\, \infty \breve{P}\infty \,.\, m\breve{P}\infty$), but appeared to consist internally of regular octohedrons.

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[*] Prepared by heating the two metals together in a covered crucible, gently at first, then more strongly, and pouring the fused mixture into cold water.

[†] Commonly said to consist of AsH^3 or As^2H^4.

Arsenious oxide dissolves abundantly in water at 250°, and the solution, as it cools, first deposits a few microscopic prisms, afterwards octohedrons. When either the vitreous or the crystalline oxide is heated in a sealed glass tube placed upright in a sand-bath, so that it is heated to about 400° in the lower, and 200° in the upper part, and then left to cool slowly, the oxide solidifies in the vitreous form at the lower part, in prismatic crystals in the middle, and in octohedrons at the upper part, a few octohedrons being also implanted on the prisms. A comparatively high temperature is therefore, at least in the dry way, an essential condition for the formation of the prismatic crystals, whereas the octohedrons are formed only at lower temperatures. In the wet way, on the other hand, the nature of the solvent appears also to exert some influence on the crystallisation, inasmuch as the oxide crystallises in prisms from its solution in potash, even at comparatively low temperatures (Debray, *Bull. Soc. Chim.* [2] ii. 9; *Jahresb.* 1864, p. 236). Nordenskiöld (*Jahresb.* 1861, p. 263) obtained it, by cooling and slow evaporation of a warm potash-solution supersaturated therewith, in six-sided trimetric crystals, $oP \,.\, \infty P \,.\, \infty \breve{P}\infty$, having the horizontal axes in the ratio of 1 to 0·5776. A solution of arsenious oxide in ammonia, saturated while hot and kept for some time at the boiling heat, the ammonia being replaced as it evaporates, deposits arsenious oxide in the rhombic modification (together with octohedral crystals); but when the same solution is left to cool slowly, the oxide is deposited in large octohedral crystals (Hirzel, *Jahresb.* 1852, p. 378). The deposition of octohedral crystals from the ammoniacal solution has also been observed by Wöhler (*Ann. Ch. Pharm.* ci. 365). According to De Luynes (*Compt. rend.* xlv. 1353), a solution of arsenious oxide in ammonia prepared at 70°–80° deposits on cooling needle-shaped crystals of ammonium arsenite, $As(NH^4)O^2$, which however gradually redissolve, if left, together with the supernatant liquid, in an open vessel, so that the ammonia can evaporate from the latter; and the liquid ultimately deposits octohedral crystals of arsenious oxide. According to Scheurer-Kestner (*Zeitschr. f. Chem.* [2] v. 487), a concentrated solution of arsenic acid supersaturated with arsenious oxide deposits the latter in acicular prisms.

Solubility.—Bacaloglo (*J. pr. Chem.* lxxxiii. 111) found that a solution of arsenious oxide saturated in the cold and left for ten months at 10°–20°, in contact with excess of the oxide, contained 1·2 p. c. As^2O^3; solutions saturated while hot contained, a few days after saturation, from 2·25 to 2·5 p. c. As^2O^3; a solution in which traces of hydrochloric acid were present contained 3·8 p. c. As^2O^3. A solution of vitreous arsenious oxide saturated while hot contained at 24°, four days after saturation, 2·4 p. c. As^2O^3; after eighty-two days, at 14°, 1·5 p. c. As^2O^3; after four months, at 12°, 1·3 p. c. As^2O^3. The presence of arsenic, phosphoric, sulphuric, and other mineral acids, increases the solubility of arsenious oxide in water. The crystals of prismatic arsenious acid from Portugal, above mentioned, were found by Claudet to dissolve in cold water to the amount of 1 p. c.; when pulverised, 1·75 p. c.; a solution saturated while hot contained after cooling 2·74 p. c.

The following determinations of the solubility of arsenious oxide in alcohol have been made by Girardin (*J. Pharm.* [3] xlvi. 269):

100 pts. alcohol of . . . dissolve:		56	79	84	86	88	100 vol. p. c.
Of the crystalline oxides:	at 15° . .	1·680	1·430	—	0·715	—	0·025 pts.
	at the boiling point. . .	4·895	4·551	—	3·197	—	3·412 „
Of the vitreous oxide:	at 15° . .	0·504	0·540	0·565	—	0·717	1·060 „

Reactions.—1. Perfectly dry arsenious oxide subjected to the action of *chlorine* at a gentle heat, gives off arsenious chloride, and leaves a sintered mass consisting chiefly of arsenic oxide, which when the heat is increased is likewise converted into arsenious chloride (R. Weber, *Pogg. Ann.* cxii. 619). According to Bloxam, the residue consists of arsenious arsenate, $2As^2O^3.As^2O^5$.—2. Heated with *sal-ammoniac* it yields arsenious chloride and ammonia, which afterwards react on one another, with formation of white fumes (Luynes, *Compt. rend.* xliv. 1354).—3. *Phosphorus pentachloride*, according to Persoz a. Bloch (*Jahresb.* 1849, p. 246), forms with arsenious oxide a definite oxychloride, boiling at 110°; but according to Hurtzig a. Geuther (*Ann. Ch. Pharm.* cxi. 159; *Jahresb.* 1859, p. 186), even when the two substances are mixed in equivalent proportions, the only products formed are arsenious chloride and phosphorus oxychloride, which separate on fractional distillation:

$$As^2O^3 + 3PCl^5 = 3POCl^3 + 2AsCl^3.$$

4. With *arsenious chloride* the oxide unites directly, forming an oxychloride, $AsClO$ or $AsCl^3.As^2O^3$ (i. 386).—5. Solutions of arsenious oxide treated with *stannous chloride*, yield stannic chloride, metallic arsenic, and gaseous hydride of arsenic (Kessler, *Jahresb.* 1861, p. 265).—6. The same solutions reduce *potassio-cupric tartrate* with separation of cuprous oxide (Terreil, *Bull. Soc. Chim.* 1862, p. 64).—7. Aqueous arsenious oxide heated to 200° with *phosphorus*, yields phosphide of arsenic (Oppenheim, *Bull. Soc. Chim.* [2] i. 163).

Combinations with other Acid Oxides.—The compound of arsenious with arsenic oxide, $2As^2O^3.As^2O^5$, which Bloxam obtained by the action of chlorine on arsenious oxide, has been already mentioned. It may also be formed by heating arsenic oxide with an excess of arsenious oxide. It is transparent at first, but solidifies after a few days to a glass, having the aspect of porcelain.

With *sulphuric oxide*, arsenious oxide forms the compound $As^2O^3.SO^3$, in small tabular crystals, which sometimes occur as a product of the roasting of native metallic sulphides containing arsenic. They deliquesce in moist air, decomposing into sulphuric acid and arsenious oxide. Heated in a tube, they are resolved into sulphuric oxide, which volatilises, and a residue of arsenious oxide (Reich, *J. pr. Chem.* xc. 176). Laurent, by heating arsenious oxide with sulphuric acid, obtained shining rectangular prisms consisting of $3(As^2O^3.SO^3).H^2SO^4$ (*J. Pharm.* [3] xlv. 184).

Acetic oxide at the boiling heat dissolves arsenious oxide in the proportion of $C^4H^6O^3$ to As^2O^3, forming a colourless syrupy liquid, which solidifies on cooling to a vitreous mass. The compound quickly absorbs moisture; is instantly decomposed by water into acetic acid and arsenious oxide; and when heated to 220° gives off a large quantity of carbon dioxide, with traces of arsenetted hydrogen, while acetic acid passes over, and metallic arsenic remains behind (Schützenberger, *Compt. rend.* liii. 538).

ARSENITES. The experiments of Bloxam (*Chem. Soc. J.* xv. 281), compared with those of other chemists, appear to show that arsenious acid is tribasic, forming

Trimetallic salts, M^3AsO^3 or $\overset{\prime\prime}{M}{}^3(AsO^3)^2$
Dimetallic salts, M^2HAsO^3 or $M''HAsO^3$
Monometallic salts, MH^2AsO^3 or $M''H^4(AsO^3)^2$.

There are also a few salts, which may be called pyro-arsenites, having the composition $2M^2O.As^2O^3$ or $M^4As^2O^5$, and acid arsenites, $M^2O.2As^2O^3$ and $2M^2O.3As^2O^3$, which may be regarded as compounds of meta-arsenites, $MAsO^2$, with free arsenious oxide:

$$M^2O.2As^2O^3 = 2MAsO^2.As^2O^3$$
$$2M^2O.3As^2O^3 = 4MAsO^2.As^2O^3.$$

Solutions of the alkaline arsenites when exposed to the *air*, gradually absorb oxygen and are partially converted into arsenates (Fresenius, *Jahresb.* 1855, p. 382; Croft, *ibid.* 1858, p. 173; Ludwig a. Macdonnell, *ibid.* 1859, p. 194; F. Kessler, *ibid.* 1861, p. 262).

Ammonium salt.—The formula NH^4AsO^2, assigned to this salt by Pasteur (*Jahresb.* 1847–48, p. 424) and by De Luynes (*ibid.* 1857, p. 269), has been confirmed by Bloxam.

The *barium salt*, obtained by adding barium chloride to a solution of arsenious oxide in ammonia, or by precipitating the sodium salt $NaAsO^2.As^2O^3$ with 1 at. barium chloride, appears to have, when dried at 100°, the composition $Ba''H^4(AsO^3)^2$ (Bloxam).

Copper salts.—On mixing a dilute solution of potassium diarsenite, $2KAsO^2.As^2O^3$, with cupric sulphate till the precipitation is complete, the precipitate dried at 100°

consists of a mixture of the salt $Cu''HAsO^3$ with arsenious oxide. The acid filtrate, mixed with an additional quantity of cupric sulphate and neutralised with ammonia, gives a precipitate consisting mainly of $Cu''HAsO^3$. The precipitate obtained with the salt $4NaAsO^2.As^2O^3$ was found to contain 2·35 at. Cu to 1 mol. of As^2O^3 and 0·92 mol. of water. Scheele's green appears to have a similar composition. Aqueous arsenious acid forms with sulphate of cuprammonium a precipitate which when air-dried consists of $Cu''HAsO^3.H^2O$, and after drying in a vacuum over oil of vitriol, of $Cu''HAsO^3$ (Bloxam).

Lead salt.—The salt $Pb^3H^6(AsO^3)^4$ is obtained by precipitating potassium diarsenite, $2KAsO^2.As^2O^3$, with lead nitrate. A *diplumbic salt* or *plumbic pyroarsenite*, $Pb^2As^2O^5$ or $2PbO.As^2O^3$ (at 100°), is formed on mixing a solution of 2 mols. lead acetate containing excess of ammonia with an aqueous solution of 1 mol. arsenious oxide.

Magnesium salt.—A cold-saturated aqueous solution of arsenious oxide is not precipitated by magnesium sulphate till after the addition of sal-ammoniac and ammonia; but precipitation then takes place, even in very dilute solutions. The precipitate dried at 100° consists of $MgHAsO^3.H^2O$; at 205°, of $MgHAsO^3$; and above 205°, of $2MgO.As^2O^3$ (Bloxam).

Potassium salts.—The acid *monopotassic salt* $2KH^2AsO^3.As^2O^3$ (or $K^2O.2H^2O.2As^2O^3$ + aq.) is obtained by digesting potassium carbonate at 100° with arsenious oxide;* it forms rectangular prismatic crystals, which give off water at 100°, and are converted into a compound of an acid pyroarsenite with arsenious oxide, $K^2H^2As^2O^5.As^2O^3$. Heated more strongly in a current of dry air, it gives off another molecule of water, and melts to a yellow liquid, which solidifies to a yellow viscous mass, consisting of a metarsenite combined with arsenious oxide, $2KAsO^2.As^2O^3$ (or $K^2O.2As^2O^3$). When potassium carbonate is boiled with arsenious oxide, the latter expels only three-fourths of the carbonic acid, and the solution when concentrated yields crystals of the salt $2KH^2AsO^3$ above described; but if the whole be evaporated at 100°, a crystalline mass is obtained, consisting of the pyroarsenite combined with metarsenious acid, $K^2H^2As^2O^5.HAsO^2$ (or $2K^2O.3As^2O^3 + 3H^2O$). This last salt does not give off its water till raised to a higher temperature, but ultimately solidifies to a crystalline mass (Bloxam).

Silver salts.—A dilute solution of the acid potassium salt KH^2AsO^3 gives with silver salts a bulky yellow precipitate, which becomes crystalline, and appears to be a mixture of the triargentic salt Ag^3AsO^3 with arsenious oxide. The filtered liquid is acid, and gives with ammonia and excess of silver nitrate a yellow precipitate of triargentic arsenite.

Sodium salts.—Arsenious oxide reacts with sodium carbonate in the same manner as with potassium carbonate, but the sodium arsenites have not been obtained in definite crystals. When the mass obtained with excess of arsenious oxide was dried at 100°, the residue exhibited the composition $Na^2O.2As^2O^3$ or $2NaAsO^2.As^2O^3$. On evaporating a solution of 3 mol. arsenious oxide with 2 mol. sodium carbonate, a black syrup was obtained, which became colourless when left to evaporate, and when dried at 100° yielded a confusedly crystalline mass of the salt $2Na^2O.3As^2O^3$ or $4NaAsO^2.As^2O^3$ (Bloxam).

Zinc salts.—A solution of zinc sulphate mixed with ammonia and sal-ammoniac and filtered, forms with a saturated aqueous solution of arsenious oxide, a bulky precipitate, which afterwards changes to microscopic spherical groups of crystals; at 100° it forms a nacreous powder, consisting of $Zn^3(AsO^3)^2$. The liquid filtered therefrom yields, on partial neutralisation with sulphuric acid, a precipitate similar in composition to the preceding; on neutralising it completely, a salt was obtained containing excess of arsenious oxide (Bloxam).

ETHYL ARSENITE. $(C^2H^5)^3AsO^3$.—Produced: 1. By the action of arsenious oxide on ethyl silicate at 220°, and separated by distillation.—2. By heating ethyl iodide with yellow silver arsenite.—3. Together with ethyl oxide, ethylene gas, and silica, by heating arsenic oxide with ethyl silicate to a temperature above 220°; on distilling the product, the ethyl oxide passes over first, then the ethyl arsenate between 150° and 200°. Ethyl arsenate is a liquid boiling without decomposition at 166°–168°, and having a density of 1·224 at 0°. Vapour-density = 7·197 at 233°; 7·380 at 267°; by calculation (2 vol.) = 7·267. It is instantly decomposed by water, with precipitation of arsenious oxide. It is not acted upon by alcohol, ether, or ethyl acetate (Crafts, *Bull. Soc. Chim.* [2] viii. 206).

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* This salt appears to be identical with Pasteur's acid salt obtained by boiling caustic potash with excess of arsenious oxide, and precipitating with alcohol (i. 377).

Arsenic Oxide, Acid, and Salts.—For the preparation of arsenic acid on the large scale, Girardin (*J. Pharm.* [3] xlvi. 269) recommends a process which consists in treating a concentrated solution of arsenious oxide in hydrochloric acid with chlorine gas, and subsequently distilling the liquid to the crystallising point.

The specific gravities of solutions of arsenic acid of various strengths have been determined by H. Schiff (*Ann. Ch. Pharm.* cxiii. 183):

Percentage of H^3AsO^4	Sp. gr. at 15°
67·4	1·7346
45·0	1·3973
30·0	1·2350
22·5	1·1606
15·0	1·1052
7·5	1·0495

Arsenic oxide treated with *phosphorus pentachloride*, yields arsenious chloride, phosphorus oxychloride, and free chlorine (Hurtzig a. Geuther, *Ann. Ch. Pharm.* cxi. 159):

$$As^2O^5 + 5PCl^5 = 2AsCl^3 + 5POCl^3 + 2Cl^2.$$

Arsenic acid boiled with very strong *hydrochloric acid* is gradually converted into arsenious chloride:

$$H^3AsO^4 + 5HCl = AsCl^3 + 4H^2O + Cl^2;$$

but with more dilute hydrochloric acid (1 pt. acid of sp. gr. 1·2 and 2 pts. water) no volatilisation of arsenic takes place (Souchay, *Zeitschr. anal. Chem.* i. 189).

Arsenic acid in solutions containing soluble chlorides is not converted into arsenetted hydrogen by the action of nascent hydrogen, as in Marsh's apparatus; but when no chlorine is present, as in a solution of ammonio-magnesian arsenate in dilute sulphuric acid, arsenic acid likewise yields arsenetted hydrogen, though less quickly and abundantly than arsenious acid. Hence the addition of sulphurous acid or hydrogen sulphide to reduce the arsenic to arsenious acid, necessary when hydrochloric acid is present, is useful also in other cases (Bloxam, *Pharm. J. Trans.* [2] iii. 607).

Arsenic acid treated in the cold with *stannous chloride*, yields a white precipitate of stannic arsenite, $2SnO^2.As^2O^3$, or stannous pyroarsenate, $Sn^2As^2O^7$ or $2SnO.As^2O^5$ (Schiff, *Jahresb.* 1861, p. 278). In warm solutions metallic arsenic is deposited and arsenetted hydrogen evolved (Kessler, *ibid.* p. 265).

Arsenates. Most insoluble arsenates are obtained by precipitation in the amorphous state, but they may sometimes be rendered crystalline by keeping them for some time at the temperature of 100°. In this manner Debray has obtained the crystallised arsenates of magnesia and zinc, $MnHAsO^4.H^2O$ and $ZnHAsO^4.H^2O$. Crystallised arsenates may also be prepared by the action of arsenic acid in solution on the corresponding carbonates. In this manner the minerals olivenite, $Cu^3(AsO^4)^2.CuH^2O^2$, and haidingerite, $CaHAsO^4 + \frac{3}{2}H^2O$, have been produced with their natural characters. Some arsenates heated with the corresponding chlorides produce arsenato-chlorides with the characters of native minerals, e.g. mimetesite, $Pb^5Cl^2(AsO^4)^4$ (Debray, *Ann. Ch. Pharm.* cxv. 50; cxxxiii. 230; *Ann. Ch. Phys.* [3] lxi. 419). Lechartier (*Bull. Soc. Chim.* [2] viii. 384), by fusing calcium arsenate with chloride and fluoride of calcium together, has obtained crystals having the form of apatite and the composition of calcium arsenato-chloride, with the chlorine partly replaced by fluorine, viz. $Ca^3(AsO^4)^2.Ca(Cl^2; F^2)$. In like manner, by fusing magnesium arsenate with chloride and fluoride of magnesium, the compound $Mg^3(AsO^4)^2.Mg(Cl^2; F^2)$ is obtained, having the form of wagnerite.

The estimation of arsenic in the arsenates of manganese, iron, zinc, lead, and copper may be easily and very exactly performed, according to H. Rose (*Pogg. Ann.* cxvi. 453), by igniting the salt, mixed with sulphur, in a covered porcelain crucible through which a stream of hydrogen is passed, till the residual metallic sulphide exhibits a constant weight. For the arsenates of nickel and cobalt, simple ignition with sulphur in the crucible suffices, but the weight of the metal cannot be calculated from that of the residual sulphide. The sulphide of cobalt, however, even after repeated treatment with sulphur, retains traces of arsenic, which can only be removed by solution in nitric acid, and ignition of the evaporated residue with sulphur. From silver arsenate also it is not possible to remove the whole of the arsenic by ignition with sulphur in a stream of hydrogen; similarly with the arsenate of aluminium, and the arsenate of magnesium and ammonium.

The arsenates of alkali-metal are easily and completely converted into chlorides by ignition with sal-ammoniac; those of the alkali-earth metals less easily; magnesium arsenate retains part of its arsenic, even after ignition with sal-ammoniac in a stream of hydrogen; so likewise do the arsenates of the heavy metals, as iron, cobalt, or nickel. Acid ammonium sulphate decomposes arsenates more easily and completely than sal-ammoniac; but the fused salt attacks the porcelain crucible so strongly that the quantity of the residual metallic sulphate comes out too high. Arsenate of magnesium and ammonium, and the arsenates of sodium, calcium, and lead, are converted into sulphates free from arsenic, even by a single fusion with acid ammonium sulphate (Rose).

Ammonium Arsenates.—The crystalline precipitate produced by adding concentrated aqueous ammonia to a solution of diammonic arsenate, $(NH^4)^2HAsO^4$, consists of the triammonic salt, and after drying between bibulous paper has the composition $(NH^4)^3AsO^4.3H^2O$ (Uelsmann, *Jahresb.* 1859, p. 185). Triammonic arsenic is likewise obtained by saturating with ammonia a solution of arsenic acid sufficiently concentrated to yield a crystalline precipitate on cooling (Salkowski, *J. pr. Chem.* civ. 129; *Bull. Soc. Chim.* [2] 447). According to Schiff (*ibid.* 16), the sp. gr. of the diammonic salt is 1·989; of the monammonic salt, $(NH^4)H^2AsO^4$, 2·249.

Barium Arsenates.—The *tribaric salt* $Ba^3(AsO^4)^2$, obtained by precipitating an ammoniacal solution of arsenic acid with barium chloride, becomes perfectly anhydrous at a little above 100°. It is nearly insoluble in water containing ammonia, more soluble in pure cold water, still more in water containing sal-ammoniac (Field, *Chem. Soc. J.* xi. 6).

The *monobaric salt* $BaHAsO^4.H^2O$ is obtained in quadratic octohedrons by dissolving precipitated amorphous barium arsenate in acetic acid, and leaving the solution to evaporate (Schiefer, *Jahresb.* 1864, p. 237). The same salt is obtained by precipitating a solution of disodic arsenate with barium chloride. By digestion with ammonia it is more or less converted into the tribaric salt $Ba^3(AsO^4)^2$. The monobaric salt dissolved in hydrochloric acid and mixed with sal-ammoniac, gives with ammonia a precipitate of an *arsenato-chloride*, $BaCl^2.3Ba^3(AsO^4)^2$ (Salkowski).

Bismuth Arsenate, $Bi'''AsO^4$, is obtained as a precipitate by adding to an acid solution of bismuth nitrate either a solution of disodic or trisodic arsenate or of arsenic acid. The whole of the bismuth is thereby precipitated, so that the reaction may be made available for the quantitative estimation of that metal. The salt dried at 100°–120° retains $\frac{1}{2}H^2O$. It is quite insoluble in nitric acid, slightly soluble in excess of bismuth salt; it dissolves in hydrochloric acid, but the solution is completely precipitated by water, and by repeating the precipitation several times the precipitate may be completely deprived of arsenic acid (Salkowski).

Cadmium Arsenates.—The salt $5CdO.2As^2O^5 + 3aq.$, or perhaps $Cd^3(AsO^4)^2, 2CdHAsO^4 + 4aq.$, is precipitated on adding disodic arsenate to cadmium sulphate. The *tricadmic salt* $2Cd^3(AsO^4)^2.3aq.$ is formed by precipitating a cadmium solution with trisodic arsenate (Salkowski).

Calcium Arsenates.—Debray (*Ann. Ch. Pharm.* cxv. 50), by digesting calcium carbonate with aqueous arsenic acid at ordinary temperatures, has obtained the salt $CaHAsO^4$ with various quantities of water according to the temperature, viz. $CaHAsO^4.1\frac{1}{2}aq.$ (haidingerite) at ordinary temperatures; $CaHAsO^4.aq.$ at 70°; $CaHAsO^4$ at 100°. Salkowski obtains this salt with 1 mol. water by precipitating calcium chloride with disodic arsenate; it gives off this molecule of water at 160°, and at 240° begins to change into pyroarsenate. On adding calcium chloride to an excess of disodic arsenate, a precipitate is formed having the more complex composition $Ca^6H^4Na^2(AsO^4)^6.8aq.$ This salt gives off $4H^2O$ at 130°. The slightly acid liquid filtered from this precipitate becomes cloudy on boiling, but clear again on cooling. On filtering it at the boiling heat, the salt $CaHAsO^4.aq.$ is left on the filter. The *tricalcic salt* $Ca^3(AsO^4)^2$ is nearly insoluble in water containing ammonia. *Ammonio-calcic arsenate*, $Ca(NH^4)AsO^4$, is easily prepared by mixing a solution of calcium chloride with a large excess of ammonia and tri-ammonic arsenate; it separates from dilute solutions in large needles, from concentrated solutions as a white crystalline powder; dried at 100° it contains $2Ca(NH^4)AsO^4.aq.$; at 140° it becomes anhydrous. It is nearly insoluble in ammoniacal water, more soluble in pure water, still more in water containing sal-ammoniac (Field).

Cupric Arsenates.—The salt $2CuHAsO^4.3aq.$ is obtained in the crystalline form by digesting cupric carbonate with aqueous arsenic acid at 70°. By digesting amorphous cupric arsenate (tribasic) with solution of cupric nitrate or sulphate, crystallised salts are obtained, viz. $Cu^3(AsO^4)^2.4aq.$ at 70°, and $Cu^3(AsO^4)^2.CuH^2O^2$ (olivenite) at a little above 100°. The last-mentioned product is obtained more distinctly crystallised by performing the digestion in sealed tubes at 150°–160°. It may also be prepared from the former hydrate, $Cu^3(AsO^4)^2.4aq.$, by digestion with water containing cupric nitrate or sulphate at 250°-270° (Debray, *Jahresb.* 1860, p. 72). Cupric sulphate precipitated by diammonic arsenate yields the salt $5CuO.2As^2O^5.3aq.$ or $Cu^3(AsO^4)^2.2CuHAsO^4.2aq.$ By adding ammonia to the mixture a cuprico-ammonic arsenate is obtained (Salkowski).

Ferroso-ferric Arsenate.—To prepare this salt, which is used in medicine, Wittstein (*Zeitschr. f. Chem.* 1866, p. 256) precipitates a solution of 3 pts. crystallised ferrous sulphate in 60 pts. water with 2 pts. dry sodium arsenate in 40 pts. water in the cold, and dries the washed white precipitate in the air on plates: it then remains in dark lumps of a deep grass-green colour, which yield an olive-green powder. The reaction is represented by the equation

$$4Fe''SO^4 + 4Na^2HAsO^4 = 4Na^2SO^4 + \overset{\prime\prime}{Fe}{}^2(AsO^4)^2 + Fe''H^4(AsO^4)^2.$$

The composition of the air-dried preparation is represented by the formula

$$2[Fe^2(AsO^4)^2.8H^2O] + 3[\overset{\prime\prime}{Fe}{}^2(AsO^4)^2.16H^2O].$$

It gives off part of its water at 100°, and the rest at a red heat, without loss of acid. The solution filtered from the precipitate gradually deposits yellowish white ferric arsenate, $\overset{\prime\prime}{Fe}{}^2(As^2O^4)^2.8H^2O$ or $Fe^2O^3.As^2O^5.8H^2O$, which when ignited leaves the brown compound $3Fe^2O^3.2As^2O^5$.

Lead Arsenates.—According to Salkowski, the salt $PbHAsO^4$ is precipitated on mixing the solutions of lead acetate and disodic arsenate. Most authorities however state that the triplumbic salt $Pb^3(AsO^4)^2$ is formed under these circumstances (i. 382).

Lithium Arsenates.—The salt $2Li^3AsO^4.aq.$ is obtained as a pulverulent precipitate by saturating arsenic acid with lithium carbonate and adding ammonia. A solution of this salt in free arsenic acid yields by spontaneous evaporation deliquescent rhombic prisms (of about 142°) of the *monolithic salt* $2LiH^2AsO^4.3aq.$, which is decomposed by water into arsenic acid and the trilithic salt (Rammelsberg, *Pogg. Ann.* cxxviii. 311; *Jahresb.* 1866, p. 160).

Magnesium Arsenate.—According to Schiefer (*Jahresb.* 1864, p. 237), the salt obtained by dissolving the residue left on igniting ammonio-magnesium arsenate in acetic acid, and leaving the solution to evaporate, has the composition $MgHAsO^4.5aq.$ A solution of magnesia in an equivalent quantity of aqueous arsenic acid yielded a crystalline highly deliquescent salt, supposed by Schiefer to consist of $MgH^4(AsO^4)^2$. According to Reischauer (*Jahresb.* 1865, p. 175), magnesium arsenate obtained by precipitation has, when air-dried, the composition $2MgHAsO^4.13aq.$, and after drying in a vacuum, $2MgHAsO^4.5aq.$

Ammonio-magnesium arsenate, $Mg(NH^4)AsO^4$, is very slightly soluble in pure water, nearly insoluble in water containing ammonia, more soluble in solution of sal-ammoniac.

From the recent experiments of Fresenius (*Zeitschr. anal. Chem.* iii. 206), it appears that 1 pt. of the salt dried at 100° ($Mg''HAsO^4.\frac{1}{2}aq.$) dissolves:

a. In 2,656 pts. water at 15°.
b. „ 15,038 „ dilute aqueous ammonia (1 pt. aqueous ammonia of sp. gr. 0·96 to 3 pts. water).
c. „ 843·9 „ concentrated solution of sal-ammoniac (1 pt. NH^4Cl to 7 pts. water).
d. „ 1,315 „ dilute solution of sal-ammoniac (1 pt. NH^4Cl to 70 pts. water).
e. „ 2,874 „ mixture of 60 pts. water, 10 pts. aqueous ammonia of sp. gr. 0·96, and 1 pt. sal-ammoniac.

Consequently 1 pt. of the anhydrous salt $Mg''(NH^4)AsO^4$ requires for dissolution the following quantities of the solvents above mentioned:

a.	*b.*	*c.*	*d.*	*e.*
2,788	15,786	886	1,380	3,014 pts.

See also Field (*Chem. Soc. J.* xi. 6).

From the observations of H. Rose (*Zeitschr. anal. Chem.* i. 413), confirmed by Wittstein (*ibid.* ii. 19), it appears that ammonio-magnesium arsenate when heated, cautiously at first, afterwards till the crucible is almost red-hot, gives up all its water and ammonia, and leaves pure dimagnesic arsenate, $Mg^2As^2O^7$ or $2MgO.As^2O^5$. In estimating arsenic by precipitation as ammonio-magnesium arsenate, the precipitate may therefore be ignited without fear of losing arsenic, and the trouble of drying the precipitate in a vacuum or at 100°, as formerly recommended (i. 367), may be saved. The process thus conducted affords the quickest and most exact of all methods of estimating arsenic.

Manganese Arsenates.—*Monomanganous arsenate*, $MnH^4(AsO^4)^2$, separates on evaporation from a solution of recently precipitated manganous carbonate in excess of arsenic acid, in deliquescent rectangular laminæ (Schiefer). Igelström (*J. pr. Chem.* xcvii. 60) describes, under the name of *Kondroarsenite*, a basic manganous arsenate, $2(5MnO.As^2O^5).5H^2O$ or $2Mn^3(AsO^4)^2.4MnH^2O^2.H^2O$, from an iron and manganese mine in Wermland, Sweden. The mineral is implanted in small yellow or reddish yellow, translucent friable grains on a heavy spar which traverses hausmannite in veins.

Nickel Arsenates.—The salts $Ni^3(AsO^4)^2$ or $3NiO.As^2O^5$ and $Ni^3(AsO^4)^2.2NiO$ or $5NiO.As^2O^5$ have been recognised by Bergemann (*J. pr. Chem.* lxxv. 239) in a mineral from Johann-Georgenstadt; the former yellow and amorphous; the latter crystalline, opaque, and brownish. The trimetallic salt has also been found by D. Forbes (*Phil. Mag.* [4] xxv. 104) in a half-decomposed greenstone (traversing the Jura beds of the Atacama Desert, about twenty leagues east of the port of Flamenco). It occurs in sulphur-yellow amorphous crusts containing 50·53 p. c. As^2O^5, 48·24 NiO, 0·21 CoO, 0·57 CuO, and 0·62 Bi^2O^3 (= 100·17).

A *nickel-cobalt arsenate*, $2(NiO;CoO).As^2O^5.8H^2O$, or perhaps $2NiHAsO^4.7H^2O$, occurs in the same locality, as a mineral of greyish-white colour, silky to resinous lustre, hardness 2·5, and sp. gr. 3·086. It gave by analysis 44·05 As^2O^5, 19·71 NiO, 9·24 CoO, and 26·98 water (= 99·98).

Potassium Arsenates.—The monopotassic salt KH^2AsO^4 has, according to Schiff, a sp. gr. of 2·832.

Silver Arsenates.—According to Kühn (*Jahresb.* 1857, p. 257), the *triargentic salt* Ag^3AsO^4 may be obtained as a dark purple crystalline precipitate, by mixing solution of silver nitrate at the boiling heat with a concentrated, almost syrupy solution of arsenic acid. This salt is soluble in arsenic acid, and the solution, kept for some days in a warm place, deposits a white crystalline powder consisting of $Ag^2O.2As^2O^5$, or a compound of argentic metarsenate with arsenic oxide, $2AgAsO^3.As^2O^5$. Water, especially if hot, decomposes this salt into arsenic acid and the normal arsenate (Hurtzig a. Geuther, *Ann. Ch. Pharm.* cxi. 159).

Sodium Arsenates.—To prepare the ordinary *disodic arsenate*, Na^2HAsO^4, on the large scale, for use as a mordant, &c., Higgins (*Dingl. pol. J.* clxxiv. 323) dissolves arsenious oxide in soda-ley, evaporates the solution mixed with sodium nitrate, and calcines the mixture in a reverberatory furnace. The solution of the residue in aqueous sodium carbonate yields on evaporation crystals of the salt $Na^2HAsO^4.12aq$. R. Wagner (*ibid.* clxxiv. 323) first prepares tricalcic arsenate by the action of iodine on a mixture of arsenious oxide and calcium hydrate:

$$As^2O^3 + 5CaH^2O^2 + I^4 = Ca^3(AsO^4)^2 + 2CaI^2 + 5H^2O;$$

then separates the dissolved calcium iodide (which is used in photography) from the undissolved calcium arsenate; and decomposes the latter by boiling with aqueous sodium carbonate. The same salt may be obtained from the arseniferous mother-liquors of the preparation of aniline red (p. 166) by adding a little sodium nitrate, evaporating to dryness, gently igniting the residue, redissolving it in water, and leaving the solution to crystallise by evaporation (E. Kopp, *Bull. Soc. Chim.* [2] ii. 158).

Sodio-ammonium Arsenate, $Na(NH^4)HAsO^4.4aq.$, may be prepared, not only by mixing the solutions of the disodic and diammonic salts (i. 384), but also by mixing the solutions of 6 pts. of the disodic salt $Na^2HAsO^4.12aq.$ with 1 pt. sal-ammoniac, leaving the liquid to crystallise by evaporation, after adding a little ammonia, and recrystallising from ammoniacal water. The concentrated solution of this salt mixed with saturated aqueous ammonia yields a precipitate consisting of faintly lustrous crystalline laminæ, which, after washing with ammoniacal water and pressure between bibulous paper, consist of the *sodio-diammonic salt*, $Na(NH^4)^2AsO^4.4aq.$ (Uelsmann, *Arch. Pharm.* [2] xcix. 138).

The specific gravities of the sodium-arsenates, as determined by Schiff (*Jahresb.* 1859, p. 16), are as follows:

$NaH^2AsO^4.aq.$	2·535	$Na^3AsO^4.12aq.$	1·762
$Na^2HAsO^4.12aq.$	1·670	$Na(NH^4)HAsO^4.4aq.$	1·838
$Na^2HAsO^4.7aq.$	1·871	$NaKHAsO^4.7aq.$	1·884

Strontio-hydric Arsenate, $SrHAsO^4.aq.$, crystallises from a solution of the precipitated salt in acetic acid, in oblique, nearly rectangular laminæ (Schiefer). According to Salkowski, strontium chloride mixed with disodic arsenate yields a precipitate of *strontio-sodic arsenate*, $SrNaAsO^4.aq.$, and the filtrate on boiling deposits *strontio-hydric arsenate*, $SrHAsO^4.aq.$

Thallium Arsenates.—See THALLIUM (v. 753, 756).

Tin Arsenates.—On adding stannous chloride in excess to an acetic acid solution of potassium arsenate, a crystalline precipitate is formed, consisting of *stannous arsenato-chloride*, $Sn^3(AsO^4)^2.SnCl^2.H^2O$, which when heated out of contact with the air suddenly decomposes, with emission of white vapours and deposition of an arsenic mirror on the sides of the vessel. By adding a small quantity of solution of stannous chloride to a concentrated acetic acid solution of potassium arsenate, a white flocculent precipitate is formed, which when air-dried has the composition of *stannous pyro-arsenate*, $Sn^2As^2O^7$ or $2SnO.As^2O^5$ (Lenssen, *Ann. Ch. Pharm.* cxiv. 113).

Zinc Arsenates.—The compound $4ZnO.As^2O^5.H^2O$ occurs native as *adamine* (p. 57). By adding disodic arsenate to zinc sulphate, a bulky amorphous precipitate is formed, consisting of the salt $5ZnO.2As^2O^5$ with $4H^2O$ at 100° and $3H^2O$ at 120°, or of $Zn^3(AsO^4)^2.2ZnHAsO^4$ with $3H^2O$ or $2H^2O$. The *trizincic salt* $Zn^3(AsO^4)^2.3H^2O$ is obtained as a gelatinous precipitate on adding trisodic arsenate to zinc sulphate (Salkowski).

ETHYL ARSENATE. $(C^2H^5)^3AsO^4$.—Prepared by heating silver arsenate in slight excess with ethyl iodide mixed with two volumes of common ether. The product is washed with ether to dissolve the ethyl arsenate, the ether driven off at 100°, in a current of carbon dioxide, and the remaining liquid is distilled under reduced pressure. Ethyl arsenate has a density of 1·326 at 0°, 1·316 at 8°. Under a pressure of 60 millimetres it distils completely between 148° and 153°; at 760 mm. it distils between 235° and 238°, but with partial decomposition towards the end of the operation, arsenic oxide being left behind. With water it forms a limpid solution which reacts like aqueous arsenic acid (Crafts, *Bull. Soc. Chim.* [2] viii. 206).

Sulphides. The precipitate formed by hydrogen sulphide in a solution of arsenic acid or of an arsenate acidulated with a mineral acid, is a mixture of sulphur and arsenious sulphide, As^2S^3, in the proportion which would produce the pentasulphide (i. 391): the sulphur may be dissolved out by carbon bisulphide. According to Fuchs (*Zeitschr. anal. Chem.* i. 189), the pentasulphide As^2S^5 may be obtained as a light yellow precipitate by mixing a dilute solution of sodium sulpharsenate with dilute hydrochloric acid. According to Flückiger, on the other hand (*Jahresb.* 1863, p. 232), the precipitate thus obtained (or with acetic acid), though it dissolves completely in ammonia, nevertheless reacts in this solution like a mixture of the trisulphide and free sulphur, inasmuch as it soon deposits sulphur and leaves on evaporation a mixture of arsenite and hyposulphite of ammonium. An ammoniacal solution of the trisulphide does not by itself deposit any sulphur, but easily takes up 2 atoms of sulphur, and then reacts as above.

Trisodic Sulpharsenate, $2Na^3AsS^4.15H^2O$ or $3Na^2S.As^2S^5.15H^2O$, is easily obtained in fine crystals by saturating a quantity of soda-ley containing 10 pts. of soda with hydrogen sulphide, and dissolving in the liquid, with aid of heat, 26 pts. of arsenious sulphide and 7 pts. of sulphur. The solution is evaporated, if necessary, till a few drops placed on a watch-glass crystallise, then filtered, and left to cool slowly; and the pale yellow crystals thus obtained are washed with a small quantity of water (Fresenius, *Zeitschr. anal. Chem.* i. 192).

ASAFŒTIDA. This gum-resin, purified by dissolving it in alcohol, distilling off the greater part of the alcohol, and precipitating the residue with water, gives off, when fused with 3 pts. of potassium hydrate, a thick aromatic vapour; and on dissolving the fused mass in water (4 pts. water to 1 pt. of potash used), acidulating the solution with dilute sulphuric acid, filtering to separate resin, and agitating the solution three times with an equal volume of ether, distilling the ethereal extracts, and evaporating, protocatechuic acid and resorcin are obtained in the proportion of 33 grms. of the former and 22 grms. of the latter to 11 ounces of the resin.

The protocatechuic acid is produced from an acid called ferulic acid, which exists ready-formed in asafœtida, and is obtained as follows: The alcoholic tincture of the resin is precipitated with an alcoholic solution of neutral lead acetate; the light yellow precipitate is freed as completely as possible from adhering resin by repeated dissolution in alcohol and pressure; and decomposed, after suspension in warm water, by dilute sulphuric acid. The filtered liquid duly concentrated yields a crystalline mass of crude ferulic acid, which, after recrystallisation from alcohol and then from boiling water, forms long, colourless, four-sided needles belonging to the rhombic system, the faces of which taper to the apex without combination-edges.

Ferulic acid is tasteless, has an acid reaction, dissolves easily in cold alcohol, not very easily in ether, scarcely at all in cold water, but completely in boiling water, very easily and with yellow colour in alcohol. The aqueous solution is precipitated by neutral lead acetate and ferric chloride; the ammoniacal solution forms with silver nitrate an egg-yellow precipitate quickly becoming darker on exposure to light. Strong sulphuric acid dissolves the crystals with yellow colour, and on heating, with brownish-red colour, the solution exhibiting a green fluorescence, which disappears on dilution with water.

The analyses of ferulic acid and of its salts lead to the formula $C^{10}H^{10}O^4$. The acid melts at 153°–154°, and solidifies in the crystalline form; fused with potash, it yields as chief product protocatechuic acid, together with small quantities of oxalic, acetic, and carbonic acids. By dry distillation it yields a viscid oil smelling like phenol and guaiacol, in which, after long standing, crystals (probably of pyrocatechin) make their appearance.

Ammonium ferulate, $C^{10}H^9(NH^4)O^4$, separates from its solution by spontaneous evaporation in laminar crystals, which give off part of their ammonia at 100°. The *potassium salt* $C^{10}H^8K^2O^4$ is straw-yellow, deliquescent, and very sparingly soluble in alcohol. The *silver salt* $C^{10}H^9AgO^4$ is a lemon-yellow precipitate soon changing colour.

ASH OF ORGANIC BODIES. E. Reichardt recommends the following process for the preparation and analysis of ashes. The substance is charred at a low red heat in a loosely covered crucible; the charcoal is rubbed to powder, repeatedly boiled out with water, and the filtrate is immediately mixed with excess of silver nitrate. The residual charcoal is then exhausted with warm water containing nitric acid, and the extract, together with the wash-waters, is mixed with the first liquid. The charcoal is next incinerated, and the ash is exhausted, first with water, then with hot strong nitric acid. These solutions are mixed with those first obtained; the mixture is acidulated, if necessary; and the precipitate, consisting of silver chloride and sulphide (the latter formed from the metallic sulphides produced in carbonisation), is collected on a filter, weighed, and dried at 100°, and treated while still moist with ammonia to dissolve the silver chloride, which compound is to be reprecipitated from the filtrate by nitric acid. The weight of the silver sulphide dried at 100° gives by calculation a part of the sulphuric acid in the ash. The residue left on treating the ash with nitric acid is warmed with strong hydrochloric acid, diluted, filtered (any insoluble portion being examined for silica), and the filtrate is mixed with that which has run from the silver precipitate. Any silver still remaining dissolved is precipitated by hydrochloric acid; the filtrate is evaporated to dryness to separate silica; and the solution obtained by digesting the dried residue with acidulated water is divided into two portions, one of which is used for the determination of sulphuric acid and alkalis, the other for the remaining constituents, according to known methods.

Soda in Plant-ashes.—To detect the presence of soda in plant-ashes, Peligot (*Zeitschr. anal. Chem.* vi. 473; *Jahresb.* 1867, pp. 763, 832) mixes the aqueous extract of the ash with baryta-water, filters, and evaporates the filtrate after having thrown down the excess of baryta by carbonic acid. The filtered liquid is then supersaturated with nitric acid and evaporated to the crystallising point, whereupon potassium nitrate crystallises out. The mother-liquor is evaporated with sulphuric acid; the strongly ignited residue is dissolved in water; and the solution, after the greater part of the potassium sulphate has crystallised out, is left to evaporate spontaneously, whereupon, if soda is absent, nothing but transparent prisms of potassium sulphate make their appearance, whereas in the contrary case, efflorescent crystals of sodium sulphate will be obtained. These latter are distinctly recognisable even when the saline mixture contains only 2 p. c. of sodium sulphate.

By this method Peligot finds that the greater number of plant-ashes do not contain sodium. Such is the case, for example, with the following plants: Wheat and oats (grain and straw); potatoes (tubers and stems); oak and white beech (wood); tobacco, mulberry, pæony, castor-oil plant (leaves); beans, vine-shoots, Parietaria, Gypsophila pubescens, Chenopodium quinoa, spinach, and parsnip. This last plant grew near others mostly belonging to the atripliceous and chenopodious families, which contain soda to a greater or less amount. In the ashes of the following plants, sodium was found (chiefly as chloride), though potassium salts predominated: Mangold-wurzel (leaves and roots), orache, Atriplex hastata, Chenopodium murale, Mercurialis annua, Zostera, and Fucus.

ASH, VOLCANIC. The following are analyses of volcanic ash from the islands of the East Indian Archipelago. Analyses by P. F. Maier: ash from the Gunung Guntur in Java, fallen, I. on January 4, 1843; II. on November 25, 1844. Analyses by Rost van Tonningen: III. ash from Merapi, fallen September 6, 1846; IV. from the volcano on Ternate, April 30, 1850; V. from the Tabucan (Tangi Islands), March

30, 1856; VI. from the Lamongau (on Probolingo), February 28, 1859; VII. from the Arosbaja (Isle of Madeira), February 28, 1859 (*Jahresb. f. Chem.* 1860, p. 808):—

	I.	II.	III.	IV.	V.	VI.	VII.
SiO^2	34·23	51·77	43·13	31·66	50·40	44·37	49·35
Al^2O^3	37·50	25·77	32·90	46·48	27·49	15·58	17·63
Fe^2O^3	18·18	13·66	10·74	14·68	12·95	29·94	22·60
CaO	6·72	7·43	7·39	4·77	5·35	8·40	7·80
MgO	0·68	0·94	2·23	0·53	0·87	0·66	0·38
X*	1·74	0·30	1·42	1·60	3·21	0·18	0·66
H^2O	0·26	0·32	1·29	0·99	1·59	0·15	0·33

The ashes do not contain either phosphates or potassium salts; their specific gravity varies from 1·572 to 2·801.

O. Prölls (*Jahresb.* 1865, p. 919) found in a volcanic ash which was ejected in large quantity on January 3 and 4, 1864, from the volcano of Kloet in Java (after deduction of 1·25 p. c. water):

SiO^2	Al^2O^3	FeO	CaO	MgO	K^2O	Na^2O
53·86	20·41	8·62	7·30	5·37	1·13	3·81

The ash was a fine, sandy, light grey powder, exhibiting, when viewed by a lens, fragments of white labradorite, dark green augite, and granules of greenish yellow olivine, but no magnetic iron ore.

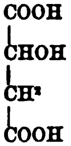
J. W. Young (*Chem. News*, xiii. 73) has analysed volcanic ash from the northern shore of the Isle of Arran, A; also two kinds of fossil wood, B and C, occurring therein:

A	SiO^2	Al^2O^3	FeO	Mn^2O^3	CaO	MgO	CO^2	H^2O	Total
a.	13·20	8·13	18·26	0·78	13·47	5·06	8·40	3·28	99·97
	SiO^2	Al^2O^3	—	—	CaO	MgO	K^2O & Na^2O	FeS^2	
b.	23·49	4·14	—	—	0·46	0·20	0·45	0·70	

a. Decomposible by hydrochloric acid. *b.* Undecomposible.

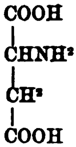
B	$CaCO^3$	$MgCO^3$	$FeCO^3$	$MnCO^3$	Fe^2O^3	Insoluble	charcoal	
	89·16	1·26	1·06	2·22	1·39	2·24	2·45	= 99·77
	SiO^2	Al^2O^3 & Fe^2O^3		CaO	MgO	Loss by ignition		
	95·30	1·00		0·73	trace	2·35		= 99·38

ASPARAGINE and **ASPARTIC ACID.** The relations of these compounds to malamide and malamic acid have already been considered under MALIC ACID (iii. 706). The following constitutional formulæ may throw additional light upon them:



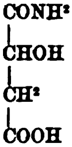
$$\begin{array}{l} COOH \\ | \\ CHOH \\ | \\ CH^2 \\ | \\ COOH \end{array}$$

Malic acid.



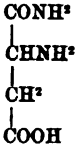
$$\begin{array}{l} COOH \\ | \\ CHNH^2 \\ | \\ CH^2 \\ | \\ COOH \end{array}$$

Aspartic acid.



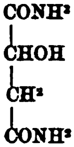
$$\begin{array}{l} CONH^2 \\ | \\ CHOH \\ | \\ CH^2 \\ | \\ COOH \end{array}$$

Malamic acid.



$$\begin{array}{l} CONH^2 \\ | \\ CHNH^2 \\ | \\ CH^2 \\ | \\ COOH \end{array}$$

Asparagine.



$$\begin{array}{l} CONH^2 \\ | \\ CHOH \\ | \\ CH^2 \\ | \\ CONH^2 \end{array}$$

Malamide.

These formulæ indicate that aspartic acid is bibasic, malamic acid and asparagine monobasic, malamide neutral. Asparagine is known to form salts by substitution of metals for one of its hydrogen-atoms. Aspartic acid was formerly regarded as monobasic, but the existence of the bimetallic aspartates obtained by Dessaignes (i. 424) clearly shows that it is bibasic. Malamide when treated with alkalis can exchange either one or both of its groups NH^2 for OH, producing, in the former case malamic acid, which is monobasic, and in the latter malic acid, which is bibasic; but asparagine, which is already monobasic, is converted by one such transformation into bibasic aspartic acid.

Asparagine occurs in considerable quantity in the expressed juice of the tubers of *Stigmaphyllon jatrophofolium*, a malpighiaceous plant indigenous in Brasil (De Luca a. Ubaldini, *Compt. rend.* lix. 527).

Buchner (*Zeitschr. f. Chem.* 1862, p. 117) prepares asparagine by subjecting the concentrated aqueous extract of marsh-mallow root to the dialytic action of parchment-paper. The liquid which runs through in the course of a day or two yields on evaporation a somewhat abundant crystallisation of asparagine. A further quantity may be obtained by renewing the water in the dialyser. By the same process Gorup-Besanez (*Ann. Ch. Pharm.* cxxv. 291) obtained from two pounds of the fresh root of *Scorzonera hispanica* about 6 grms. of pure asparagine.

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* Soluble salts, sodium chloride, sulphate, &c.

A cold saturated solution of asparagine is gradually oxidised, with rise of temperature, by potassium permanganate, yielding, as chief products, ammonia, formic acid, carbon dioxide, and hydrocyanic acid:

$$C^4H^8N^2O^3 + O^4 = CH(NH^4)O^2 + 2CO^2 + CNH + H^2O.$$

In presence of sulphuric acid the oxidation takes place according to the equation:

$$C^4H^8N^2O^3 + O^6 = 2NH^3 + 4CO^2 + H^2O;$$

in presence of potash, thus:

$$C^4H^8N^2O^3 + O^4 + 4KHO = 2NH^3 + 2C^2K^2O^4 + 3H^2O,$$

neither carbonic nor hydrocyanic acid being formed in this case (Campani, *Zeitschr. f. Chem.* [2] vi. 87).

Aspartic acid is contained in somewhat considerable quantity in the juice of mangold-wurzel which has been treated with lime, and especially in the molasses (being formed therein by the decomposition of asparagine). To obtain it, the moderately dilute solution is precipitated with basic acetate of lead; the filtrate is mixed with mercurous nitrate; the impure mercurous aspartate thereby precipitated is decomposed by hydrogen sulphide; the filtrate is evaporated to a syrup; and the acid which crystallises out is purified by boiling with moderately strong alcohol, and recrystallisation from alcohol. The presence of aspartic acid in the beet-juice is a source of error in the estimation of the sugar by the polariscope, inasmuch as alkaline solutions of asparagine and aspartic acid are lævogyrate, acid solutions dextrogyrate (C. Scheibler, *J. Pharm.* [4] iv. 152). In the beet-molasses of the years 1867 and 1868, Scheibler has found, instead of aspartic acid, an acid having the composition of its next higher homologue, $C^5H^9NO^4$ (*Deut. Chem. Ges. Berlin.* 1869, 296).

Aspartic acid is produced (together with leucine and tyrosine) when animal proteides are boiled with sulphuric acid (Kreusler, *Zeitschr. f. Chem.* [2] vi. 93); also, together with glutamic acid, by boiling legumin or conglutin with sulphuric acid (Ritthausen, *ibid.* 126).

When dry acid barium aspartate is distilled with potassium ethylsulphate, alcohol is given off, and the residue contains, together with the sulphates of barium and potassium, a substance $C^4H^5NO^3$, which is also produced in the dry distillation of acid ammonium malate:

$$Ba''(C^4H^6NO^4)^2 + 2C^2H^5KSO^4 = 2C^4H^5NO^3 + 2C^2H^6O + BaSO^4 + K^2SO^4.$$

If the potassium sulphate be first dissolved out by water, the residue treated with hydrochloric acid, and water added to the resulting solution, a tasteless compound is obtained, insoluble in water and converted by boiling with hydrochloric acid into hydrochloride of aspartic acid (Dessaignes, *J. Pharm.* [3] xxxii. 49).

ASPEROLITE. A copper silicate from Tagilsk, so called on account of its brittleness. It forms kidney-shaped amorphous masses, having a vitreous lustre, blue-green colour, and conchoïdal fracture; hardness = 2·5; sp. gr. = 2·306. Easily decomposed by hydrochloric acid, with separation of pulverulent silica. Contains 31·94 p. c. SiO^2, 40·81 CuO, and 27·25 water, agreeing with the formula $CuSiO^3 . 3H^2O$ or $CuO . SiO^2 . 3H^2O$. This mineral forms therefore the third member of the series of hydrated cupric metasilicates, the first term of which is formed by dioptase, $CuSiO^3 . H^2O$, and the second by chrysocolla, $CuSiO^3 . 2H^2O$ (R. Hermann, *J. pr. Chem.* xcvii. 352).

ASPHODELUS. The root of *Asphodelus Kotschy* (*Rad. Carniolæ*), indigenous on the Antilebanon and Gauran, has been examined by Dragendorff (*Zeitschr. f. Chem.* 1865, p. 734), in comparison with salep-root. The following are the results:

Radix Carniolæ.	p. c.
Dextrin (with a little arabin)	20·9
Arabin (with a little dextrin)	31·2
Insol. vegetable mucilage (cutin)	10·0
Sugar	3·8
Cellulose	4·6
Protein substances	4·3

Salep-root.	p. c.
Dextrin, arabin, and half-soluble vegetable mucilage	48·1
Starch	27·3
Sugar	1·2
Cellulose	2·4
Protein substances	4·9

The ash of *Rad. Carniolæ* (A), amounting to 4·8 p. c., and that of salep-root (B), to 2·1 p. c., exhibited the following composition:

	A.	B.
K^2O	30·192	23·134
Na^2O	0·903	9·327
CaO	21·436	20·659
MgO	4·818	3·903
Fe^2O^3	0·323	0·722
SO^3	3·718	2·803
Cl	2·968	12·820
P^2O^5	4·606	28·792
CO^2	13·877	2·751
SiO^2	4·048	6·644
Insoluble	6·634	

ASPIDIUM FILIX MAS. Pavesi (*Arch. Pharm.* [2] cviii. 142) obtained from the root of this fern a thickish, oleo-resinous, yellowish mass, having a sharp bitter taste, insoluble in water, ammonia, potash, and soda, not attacked by dilute nitric, hydrochloric, or acetic acid, but soluble in alcohol and ether. To this substance, which he designates as aspidin, Pavesi ascribes the anthelmintic action of the root.

The ash of male fern root (freed from the leafy scales, but still covered with the brown epidermis) amounts, according to Spiess (*Chem. Centr.* 1860, p. 766), to 2·74 p. c. of the root dried at 100°. Its analysis gave 6·78 p. c. K^2O, 1·17 Na^2O, 37·73 CaO, 1·27 MgO, 2·67 Fe^2O^3, 0·07 Al^2O^3, 14·87 P^2O^5, 8·48 SiO^2, 9·08 SO^3, 3·83 Cl, 12·80 CO^2 with 0·25 loss.

ASTACUS. The blood of the crawfish, *Astacus fluviatilis*, is, when it first flows out, colourless, limpid, mobile, very slightly alkaline, and gives with acetic acid a precipitate soluble in excess of that reagent. It coagulates to a jelly on exposure to the air, or when boiled, and consequently forms a clot and serum, like the blood of vertebrate animals; the clot consists of a substance resembling fibrin; the serum contains albumin. The blood contains 90·89 p. c. water, 1·55 salts, and 7·56 organic matter. The alkaline ash, free from carbonic acid, contains, in addition to the usual constituents of blood-ash, 2·49 p. c. cupric oxide (E. Witting, *J. pr. Chem.* lxxiii. 121).

The colouring matter of the crawfish is greenish-blue, with red patches, and in animals with comparatively old shells it is deposited between the shell and a thin membrane on the knobby parts of the shell; it is turned purple-red by ammonia. In crawfish with soft shells, the blue or brown-green colouring matter is situated upon or under a soft membrane between the shell and the flesh. The colouring matter dissolves in alcohol with bluish colour changing to red; it is turned crimson by ammonia, brick-red by acetic acid, or by boiling with water. The red colour produced by alkalis is destroyed by hydrochloric and by nitric acid: hence the brownish-green colour is perhaps the original (Witting, *loc. cit.*).

ASTROPHYLLITE. This mineral, occurring in the zircon-syenite at Barkevig on the Brevig fjord in Norway, accompanied by a black mica, an augite allied to ægyrin, also zircon, catapleiite, palæo-natrolite, elæolite, sodalite, cancrinite, and other minerals, has been analysed: *a*, by Pisani (*Compt. rend.* lvi. 846); *b*, by Scheerer, *Pogg. Ann.* cxxii. 107; *c*, by Meineke (*ibid.*); *d*, by Sieveking (*ibid.*).

	a.	*b.*	*c.*	*d.*
Silica	33·23	32·21	32·35	33·71
Titanic oxide	7·09	8·24	8·48	8·76
Zirconia	4·97	—	—	—
Alumina	4·00	3·02	3·46	3·47
Ferric oxide	3·75	7·97	8·05	8·51
Ferrous oxide	23·58	21·40	18·06	25·21
Manganous oxide	9·90	12·63	12·68	10·59
Lime	1·13	2·11	1·86	0·95
Magnesia	1·27	1·64	2·72	0·05
Potassium oxide	5·82	3·18	2·94	0·65
Sodium oxide	2·51	2·24	4·02	3·69
Lithium oxide	trace	—	—	—
Water	1·86	4·41	4·53	4·85
	99·11	99·05	99·15	100·44

From the last three analyses Scheerer deduces the formula $3(3MO.2SiO^2) + M^2O^3.2SiO^2$, which, if M^2O^3 be equivalent to $3MO$, may be reduced to $3MO.2SiO^2$. The mineral appears therefore to differ in composition from ordinary mica, and, according to Scheerer's observation (*Jahresb.* 1855, p. 951), it also differs from mica in crystalline form, exhibiting the monoclinic combination $oP . [\infty P\infty] . P3 . \frac{1}{2}P\infty$, and always without the prism ∞P of nearly 120° which occurs constantly in mica. The crystals cleave parallel to oP, and are always elongated in the direction of the clinodiagonal. Twins occur; also stellate and cauliflower-like groups of radiate crystals. According to Descloizeaux, astrophyllite also differs from normal mica in its optical characters. It is brown-black, bronze-brown to brownish-golden yellow with metallic vitreous lustre. Sp. gr. 3·3 to 3·4. Tschermak (*Jahresb.* 1863, p. 321) regards astrophyllite as a somewhat altered anthophyllite.

ATACAMITE. This mineral occurs very abundantly in the copper mines of Algoden Bay in Bolivia. Selected crystalline splinters analysed by v. Bibra (*J. pr. Chem.* xcvi. 193; *Jahresb.* 1865, p. 913) gave the following results:

CuO	Cu	Cl	H^2O		Total
52·54	13·33	14·96	19·17	=	100
53·65	14·75	16·56	15·13	=	100·09
50·32	14·55	15·90	19·23	=	100
52·40	14·00	15·07	18·53	=	100

Tschermak (*Chem. Centr.* 1865, p. 616) observed on crystals of atacamite the forms $\infty P, \breve{P}\infty, \infty\bar{P}\infty, P, oP, 2\breve{P}2$. He finds that the atacamite sand of Chile always contains a perceptible quantity of sulphuric acid, arising from brochantite.

Respecting the formation of atacamite, see Field (*Chem. Gaz.* 1858, p. 430; *Phil. Mag.* [4] xxiv. 123).

ATHEROSPERMA. The bark of *Atherosperma moschatum* has been examined by N. Zeyer, who has found in it volatile oil, fixed oil, wax, albumin, gum, sugar, starch, butyric acid, oxalic acid, an aromatic resin, iron-greening tannic acid, and an alkaloïd, which he designates as atherospermine. The lead-compound of the tannic acid was obtained by precipitating the clarified aqueous decoction of the bark with lead acetate, digesting the well-washed precipitate with acetic acid, and exactly saturating the filtrate with ammonia. The greyish-yellow precipitate thus formed gave by analysis, after drying, numbers answering to the formula $C^{16}H^{14}Pb''O^8$.

When the bark, after being boiled out with water and treated with dilute sulphuric acid, is exhausted with weak soda-ley, the aromatic resin passes into solution, and may be separated by precipitation with hydrochloric acid, and purified by treatment with alcohol and water. It is brown-red, has a faint aromatic odour, tastes distinctly like nutmeg and sassafras, melts at 114°, dissolves easily in alcohol and in alkaline hydrates and carbonates, with difficulty in ether and in turpentine oil. The analysis of the resin gave numbers according with the formula $C^{21}H^{22}O^3$ (Zeyer, *Jahresb.* 1861, p. 769).

The ash, amounting to 3·64 p. c. of the air-dried bark, and 4·06 p. c. of the bark dried at 100°, was found by Zeyer to contain 2·675 p. c. NaCl, 4·036 K^2O, 8·321 Na^2O, 45·445 CaO, 4·361 MgO, 0·191 Al^2O^3, 0·098 Fe^2O^3, 0·477 Mn^2O^3, 1·442 SO^3, 1·186 P^2O^5, 1·396 SiO^2, and 30·005 CO^2.

The volatile oil (called *Victoria sassafras* oil), obtained by distilling the dried bark, is pale yellow, has a peculiar odour, distils almost wholly at 224°, and has a sp. gr. of 1·0425 at 15·5 (Gladstone). Respecting its optical properties, see OILS, VOLATILE (iv. 186).

ATHEROSPERMINE. The solution filtered from the impure lead-precipitate mentioned in the last article yields, on addition of ammonia, a precipitate, which, after washing and drying, digestion with alcohol, evaporation of the brown solution, mixing of the remaining mass with hydrochloric acid, and precipitation with ammonia, yields crude atherospermine; and by agitating this substance with carbon bisulphide, dissolving the mass left after evaporating off the carbon bisulphide in hydrochloric acid, and again precipitating with ammonia, the atherospermine is obtained in the pure state.*

Atherospermine forms a white, somewhat greyish, light, highly electric powder, inodorous, and having a pure bitter taste. It turns yellowish when exposed to sunshine, melts at 128°, and at a higher temperature emits an empyreumatic odour, takes fire, and burns away without residue; when slowly heated it gives off an odour of putrid meat, and afterwards of herrings (propylamine?). It is nearly insoluble in water, dissolves with difficulty in ether, more easily in alcohol, the solution having a distinct alkaline reaction; soluble also in chloroform, oil of turpentine, and other volatile oils. When dissolved in dilute acids, it neutralises them, with formation of varnish-like salts. In contact with iodic acid and a little water, it liberates iodine with brown colour. The neutral solution of the alkaloïd in hydrochloric acid is precipitated white by alkalis and alkaline carbonates, yellow by picric acid, yellowish white by tannic acid, dirty yellow by phosphomolybdic acid, pale yellow by platinic chloride; it likewise yields precipitates with iodide, ferrocyanide, and sulphocyanate of potassium, auric chloride, &c. The formula of atherospermine has not yet been determined (Zeyer, *loc. cit.*).

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* The bark which had been boiled with water for the preparation of the tannic acid still retained a portion of the alkaloïd, which was extracted therefrom by digestion with dilute sulphuric acid.

ATMOSPHERE. 1. *Variation in the amount of Carbon dioxide.*—Ch. Méne (*Compt. rend.* lvii. 155) infers, from a series of determinations made by passing air through baryta-water of known strength, and subsequently titrating the baryta with standard hydrochloric acid, that the proportion of carbon dioxide in the air varies at different seasons, being constant in December and January, increasing in February, March, April, and May, decreasing from June to August, increasing again from September till November, and attaining its maximum for the whole year in October. During the night the air contains more carbon dioxide than in the daytime, and even during the day it is not quite constant, a slight increase occurring about noon. The quantity is also slightly increased after rain.

From the observations of Lewy (*Ann. Ch. Phys.* [3] xvii. 5), made upon the air over the Atlantic Ocean, it had been concluded that air over the sea contains a larger proportion of carbon dioxide than that over the land, and that sea-air is richer in carbon dioxide during the day than during the night, the mean results obtained being 5·299 pts. in 10,000 for the day, and 3·459 pts. for the night. The observations of T. E. Thorpe, however (*Chem. Soc. J.* [2] v. 189), made on the air of the Irish Sea and of the Atlantic Ocean, have led to totally different conclusions. The mean of 26 determinations of the air over the Irish Sea (made in the month of August at 4 A.M. and 4 P.M.) gave 3·086 vols. carbon dioxide in 10,000 vols. of air (minimum 2·92; maximum 3·32). The air over the Atlantic Ocean was found to contain in 10,000 vols. a mean amount of 3·011 vols. carbon dioxide during the day (min. 2·85; max. 3·17); during the night 2·993 vols. (min. 2·70; max. 3·26); as the mean of the whole 51 experiments, 2·953 vols.; and as the general average of the results obtained over the ocean and over the Irish Sea, 3·00 vols. Hence it appears to be established that the proportion of carbon dioxide in sea-air, in various latitudes and at different times of the year, is nearly constant, does not vary perceptibly at different times of the day and night, and is always considerably less than in the air over the land, which, according to the general mean of the most trustworthy observations, is 4·04 p. c. The sea cannot therefore have any tendency to increase the proportion of carbon dioxide in the land-air. The higher results obtained by Lewy are attributed by Thorpe to the methods of analysis (Regnault's eudiometric method) which he employed. Thorpe's observations were made by Pettenkofer's method (absorption of the carbon dioxide by lime-water of known strength, and subsequent titration of the lime-water with oxalic or hydrochloric acid).

Thorpe has also determined the proportion of carbon dioxide in the air of tropical Brazil, at Para, 80 miles from the sea, on the borders of an extensive primeval forest, on the river Gram-Para, lat. 1° 27′ S., long. 48° 28′ W. The observations, made during the rainy season (April and May 1866), gave in 10,000 vols. of air, a minimum of 3·07 vols. carbon dioxide, maximum 3·49 vols., or as a mean of 31 determinations made on 17 days, 3·28 vols. carbon dioxide. This mean value is considerably lower than that determined by Lewy (*loc. cit.*) for the land-air of the tropics (3·822 in the rainy season, 4·573 during the dry season), and than the mean amount of the land-air in Europe. The difference is probably due to the united action of the tropical rains and of the luxuriant vegetation (*Chem. Soc. J.* [2] v. 199).

A. McDougall (*Chem. News*, ix. 30) has determined, under Roscoe's direction, the amount of carbon dioxide in the air of Manchester and its environs. On two different days the amount in 10,000 vols. of air was found to be:

	In Manchester	Four miles from Manchester
I.	3·90	3·85
II.	2·80	2·77

As the mean of 46 determinations, 10,000 vols. air from the centre of Manchester were found to contain 3·92 vols. carbon dioxide (min. 2·8; max. 5·6); the air outside the town contained, as a mean of eight determinations, 4·02 vols. From these results Roscoe concludes that in open places the influence of combustion and respiration processes is completely neutralised by the movements of the air.

R. Angus Smith, in an elaborate report on the air in mines and other confined places (London, 1864), has published numerous experiments on the amount of oxygen, carbon dioxide, and dust in the air, the causes of its deterioration, and the influence of its alterations on the health of workmen. Taking as a standard air containing 20·9 vols. p. c. oxygen, Smith regards air containing 20·6 p. c. as decidedly impure, and air containing 20·5 p. c. as very bad, and dangerous if inhaled for any considerable time; air containing only 17·2 p. c. oxygen is difficult to endure even for a few minutes. In 10·7 p. c. of 393 samples of air from metal and coal mines, the proportion of oxygen was nearly normal; 24·7 p. c. were impure, and 64·6 p. c. very bad. The smallest amount of oxygen found in air from mines was 18·97 p. c.; the mean amount of carbon dioxide, 0·785 p. c. In closed ends of mines, in consequence of the combustion of illuminating material and of blasting powder, and of the respiration of the miners, the proportion of carbon dioxide sometimes reaches 2·1 p. c. The quantity of solid matter which, in the form of dust from the rock, and from the combustion of the powder, is inhaled by a workman in the course of a day amounts to about 90 grains.

In a well-ventilated room lighted with petroleum Smith found 20·84 p. c. oxygen, and after the lamp had burnt for six hours, 20·83 p. c.; in the pit of a theatre at half-past eleven in the evening, 20·74 p. c.; in the gallery, 20·36 p. c.

Ammonia.—A. Müller, by exposing dilute sulphuric acid to the air in shallow vessels placed in an elevated open situation, but protected from rain, found that it absorbed in four months only 28 milligrams of ammonia for every square foot of surface, corresponding to rather more than 4 kilograms per hectare (*J. pr. Chem.* xcvi. 339).

In 1016 litres of the air of stables in which horses were kept, Clemm a. Erlenmeyer (*Zeitschr. f. Chem.* 1860, p. 52) found 0·0394 grms. ammonium carbonate, and 0·693 grms. of free carbon dioxide.

Saline particles.—Sodium salts, especially the chloride, are so constantly present in atmospheric dust that it is difficult to obtain a flame-spectrum in which the yellow sodium line is not more or less apparent. This dust of sodium salts is derived from the evaporation of the minutely divided particles of sea-spray, and from the transportation of the minute solid particles by the winds (v. 379). Gernez (*Compt. rend.* lxi. 289), by passing air in the open country through water which had been twice distilled from a platinum retort and collected in a platinum condenser, and then leaving a few drops of the water to evaporate on a glass plate, obtained efflorescent crystals of sodium sulphate recognisable by the microscope. According to Barral (*Compt. rend.* li. 769), atmospheric air also contains phosphorus-compounds. In the residue obtained by evaporating rain-water collected in platinum vessels, he found from 0·05 to 0·9 milligrams phosphoric oxide (P^2O^5) to the litre of rain-water, the amount being nearly the same whether the water was collected in the neighbourhood of Paris or in the country. De Luca (*Compt. rend.* lii. 1021), by observations made in Pisa in 1860–61, found that all the rain and snow-water there collected contained variable quantities of inorganic salts, nitrogenous organic matters, and nitric acid. The water collected at 54 and at 18 metres above the surface contained neither phosphates nor iodides, whereas these substances could be easily, though not always, detected in water collected near the surface.

Ozone.—As ordinary oxygen is known to be converted into ozone under the influence of electricity, and of a number of slow oxidising actions which are constantly taking place on the surface of the earth, it appears probable that ozone will be found to exist in the atmosphere, if not constantly, at least at certain times and in certain places. And in fact certain oxidising actions do take place on bodies exposed to the air, which are known to be produced by ozone, but not by ordinary oxygen: for example, the blueing of starch-paper impregnated with potassium iodide, the brown coloration of manganous sulphate, and the oxidation of black sulphide of lead into white sulphate (iv. 302). It has even been supposed that atmospheric ozone destroys the putrid miasmata and minute organisms which often render the air unhealthy; and observations made in India have indicated a relation between the diminution of the amount of ozone in the air and the increase of cholera, dysentery, and intermittent fevers in certain localities.

It has, however, been objected that the blueing of iodised starch-paper, and other oxidising actions attributed to ozone, may also be produced by nitrous acid and other oxygen-compounds of nitrogen, which are known to exist frequently, if not always, in the air, and that therefore these reactions cannot be looked upon as affording proof of the existence of atmospheric ozone, unless the action of the nitrogen oxides can be eliminated, or unless the evidence can be corroborated by other reactions which these nitrogen-compounds are not capable of producing (Cloez, *Compt. rend.* xliii. 38; lii. 527; *Jahresb.* 1856, p. 267; 1861, p. 163. J. Piess a. V. Pierre, *Wien. Akad. Ber.* xxii. 211; *Jahresb.* 1857, p. 79. Zenger, *Wien. Akad. Ber.* xxiv. 78; *Jahresb.* 1857, p. 79).

In reply to these objections, Houzeau has shown (*Compt. rend.* xlv. 873; xlvi. 89; *Jahresb.* 1857, p. 80; 1858, p. 61) that a neutral solution of potassium iodide exposed to the air in the open country, but protected from sun and rain, becomes alkaline, and exhibits after some time a diminished proportion of iodine, the potassium being in fact converted into potash by the oxidising action of ozone, while the iodine is set free and gradually escapes. That the alkalinity was not due to the absorption of ammonia by the solution, or to the falling in of alkaline dust, was shown by the fact that the solution did not lose its alkalinity when heated, and that distilled water placed side by side with the solution of potassium iodide did not become alkaline; it is evident also that the alkalinity could not arise from decomposition of the potassium iodide by nitrous acid.

Further, by comparative observations on the air at Paris, at Rouen, and in the open country, Houzeau has found that the colouring of potassium iodide solution, and of iodised starch-paper, takes place less strongly in proportion as the presence of acids in the air (indicated by permanent reddening of litmus-paper) becomes more perceptible (*Compt. rend.* lxi. 40; *Jahresb.* 1865, p. 122).

To detect ozone in the air, Houzeau passes the air first through water slightly coloured with wine-red tincture of litmus, and then through a similarly coloured solution of neutral potassium iodide. If the air contains ozone, but no nitrous acid, the colour of the latter solution changes to brownish- or yellowish-blue, while that of the water remains unaltered; if, on the other hand, the action of the ozone in the air is complicated by that of oxygen-acids of nitrogen, their presence is indicated by the reddening of the coloured water. For the quantitative estimation of ozone in the air, Houzeau passes it through a very dilute solution of potassium iodide containing a known quantity of sulphuric acid; afterwards expels the free iodine by boiling the liquid till it is decolorised; and estimates by titration the quantity of potash which has been set free by the ozone and partially neutralised by the sulphuric acid.

Paper soaked in solution of *thallious oxide* is recommended by Böttger (*J. pr. Chem.* xcv. 111) as the best reagent for the detection of ozone, because it is turned brown by ozone, but not affected by nitrous acid. According to Huizinga (*ibid.* cii. 193), it is even bleached by nitrous acid if previously coloured brown by ozone; accordingly the browning of thallium paper exposed to the air will in most cases be only the difference between the two opposite actions of ozone and nitrous acid, and sometimes will not take place at all, in consequence of the action of the latter equalling or exceeding that of the ozone (see also Schönbein, *J. pr. Chem.* ci. 321).

Andrews (*Phil. Mag.* [4] xxxiv. 315; *Jahresb.* 1867, p. 179) has shown that the constituent of the air which separates iodine from potassium iodide exactly resembles ozone in its action upon metallic mercury and manganese dioxide, and more especially in its behaviour when heated. Ozone is reconverted into ordinary oxygen at 237° (iv. 301), and active atmospheric air becomes inactive at the same temperature. When active air is passed at the rate of 3 litres per minute through a glass globe of about 5 litres capacity, and then through a U-tube a metre long connected therewith, and moistened within, iodised starch-paper held in the escaping current of air is turned blue so long as the apparatus is not heated; but if the globe be heated to 260°, while the U-tube is kept cool by immersion in cold water, the paper is no longer turned blue. Ozone is also reconverted into ordinary oxygen by contact with peroxides; and, in like manner, active atmospheric air passed over manganese dioxide loses its power of decomposing potassium iodide. Lastly, active atmospheric air oxidises metallic mercury in the same manner as electrolytic ozone; but this reaction is less characteristic and more difficult to recognise than those above mentioned.

Daubeny (*Chem. Soc. J.* [2] v. 1) also concludes, from a long series of observations carried on at Torquay and at Oxford, that the constituent of the atmosphere which separates iodine from potassium iodide cannot be either nitrous acid or chlorine, inasmuch as it bleaches litmus without previously reddening it, and does not produce turbidity in a solution of silver nitrate. On the other hand, he found that the action of light may introduce a serious error in ozonometry, inasmuch as mere exposure to direct sunshine colours paper dipped in iodised starch or in manganous sulphate, in the same manner as ozone, and even diffused daylight perceptibly strengthens the coloration produced by ozone. Hence for exact determinations of the strength of the ozone reaction the sensitive papers should be exposed to the air in a dark vessel. Observations made on numerous species of plants, with attention to this circumstance, have shown that the green parts of plants, when exposed to light, give out, in addition to ordinary oxygen, small quantities of active oxygen, and consequently that vegetation must be regarded as one of the most productive sources of atmospheric ozone.

A. Cossa (*Zeitschr. anal. Chem.* vi. 24) recommends that, for the exact estimation of ozone, the air should be passed first through potash-ley (to absorb nitrous acid, &c.), then through a solution of potassium iodide, and the separated iodine determined volumetrically.

Bérigny a. Sallérin (*Compt. rend.* lxv. 982) propose to determine the time during which ozonoscopic paper must be exposed to the air, in order that when subsequently moistened it may acquire a normal colour (the fourth tone of the first violet in Chevreul's circle of colours). For this purpose they cause the paper to be rolled on a cylinder by clockwork, so that for each division the time of exposure may be known. This mode of observation is designated as chronozometry.

Variations in the Amount of Atmospheric Ozone.—From observations made by Houzeau (*Compt. rend.* lx. 788) at Rouen in the years 1861 to 1864, it appears that the greatest number of days per month on which the air exhibited indications of ozone fell in the months of May and June; in the later summer months and in autumn the presence of ozone was less frequent, and in winter it attained its minimum, increasing again in March. The quadrennial average of days on which ozone was perceptible was 22 days from January to March, 56 from April to June, 37 from July to September, and 19 from October to December, A. Bérigny (*Compt. rend.* lx. 903), from a nine years' course of observations made at Versailles from 1856 to 1864, came to a general conclusion which agrees to a considerable extent with that of Houzeau. Bérigny observed the absolute maximum to occur in May, the absolute minimum in November and February. All the separate (monthly) maxima were observed to coincide with storms occurring in the neighbourhood or in a perfectly determinate direction; the minima, most frequently at least, with more distant storms (see also Houzeau, *Compt. rend.* lxii. 426). M. Böckel (*Ann. Ch. Phys.* [4] vi. 235) also concludes, from observations continued for eleven years at Strasburg, that the air is richer in ozone in spring than during the rest of the year. He finds that the month of May is the richest in ozone, while October and November are the poorest. In the first six months of the year, and from October to December, the proportion of ozone in the air is smaller in the evening than in the morning, whereas the opposite relation is observed in July, August, and September. The maxima of ozone occur especially in the first five and the last two months of the year; the minima in the first two and the last three. Many years are exceptionally rich in ozone. Böckel further directs attention to certain relations between the mean height of the barometer and the mean amount of ozone in the air in particular months; within certain limits these two magnitudes appear to be inversely proportional one to the other.

ATOMIC VOLUME. *Specific Volume.*—H. Kopp showed some years ago that the atomic volume of a compound depends, not merely on its molecular weight, but also on its constitution as represented by the rational formula (i. 448). An additional example of this relation is afforded by the isomeric bodies, aldehyde, $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O$, and ethylene oxide, $(C^2H^4)''O$. According to the previously established atomic volumes of oxygen, in its intra-radicle and extra-radicle position, these two bodies should have different atomic volumes, and consequently different specific gravities. The calculated atomic volume of aldehyde for 0° is 54·3; that of ethylene oxide 50·6, assuming that these two bodies undergo equal contractions for equal decrements of temperature from their boiling points. Consequently the calculated sp. gr. of aldehyde (quotient of atomic weight by atomic volume) is $\frac{44}{54{\cdot}3} = 0{\cdot}810$; that of ethylene oxide $\frac{44}{50{\cdot}6} = 0{\cdot}870$. Now from actual determinations by Wurtz, it appears that the sp. gr. of aldehyde at 0° is 0·807; that of ethylene oxide 0·895–0·898 (Kopp, *Ann. Ch. Pharm.* cxxviii. 193).

The researches of Marignac have shown that isomorphism may exist between compounds containing equal numbers of atoms of elements not of equal atomicity or combining capacity (p. 237), as for example in $CuTiFl^6$ and $CuWO^2Fl^4$ (iv. 786; v. 902). Such isomorphous compounds thus related have been further shown by Kopp (*Ann. Ch. Pharm.* cxxv. 371; *Jahresb.* 1863, p. 3) to be at least approximately equal in their atomic volumes, as in the following instances:

		Atomic weight	Spec. gravity	Spec. volume
Copper glance	$CuCuS$	158·8	5·71	27·8
Argentiferous copper glance . .	$CuAgS$	203·4	6·26	32·5
Potassium perchlorate . . .	$KClO^4$	138·6	2·54	54·6
Potassium permanganate . . .	$KMnO^4$	158·1	2·71	58·3
Potassium nitrate	KNO^3	101·1	2·11	47·9
Barium carbonate	$BaCO^3$	197·0	4·30	45·8
Sodium nitrate	$NaNO^3$	85·0	2·24	37·9
Calcite	$CaCO^3$	100·0	2·72	36·8

In some cases, however, as in anorthite and other complicated minerals, in which the alkali-metals appear to be isomorphously replaced by calcium, such replacement takes place, not in atomic, but in equivalent proportions, e.g. 39 pts. potassium by 20, not by 40 pts. of calcium.

A certain relation between the atomic volumes of similarly constituted compounds and their volatility has been pointed out by J. Persoz (*Compt. rend.* lx. 1126; *Jahresb.* 1865, p. 33). In compounds derivable from one another by substitution, the boiling point becomes lower as the atomic volume increases, the highest boiling points corresponding for the most part to the greatest densities. Thus the atomic volume of chlorine-compounds is greater than that of the (less volatile) oxides; that of the mercaptans is greater than that of the (less volatile) alcohols; the atomic volume of ethyl alcohol at the boiling point is to that of mercaptan as 14 to 17; that of amyl alcohol to that of amylic mercaptan as 39 to 56.

As the molecules of bodies in the state of gas or vapour occupy for the most part equal volumes, it follows that the molecular equations which represent double decompositions between bodies capable of assuming the gaseous state must also be volume-equations; that is to say, in any such reaction the sum of the molecular volumes of the acting bodies must be equal to the sum of the volumes of the products in the state of gas or vapour. The existence of a similar relation in the double decompositions of liquid and solid bodies has been pointed out by Mendelejef (*Jahresb.* 1858, p. 29) and by Semenoff (*ibid.* 1865, p. 30). Thus:

Formation of Barium Nitrate.

	$2NO^3H$ +	BaH^2O^2	Sum	$(NO^3)^2Ba$ +	$2H^2O$	Sum
Mol. weight	126	171	—	261·18	26	—
Sp. gr. . .	1·552*	4·495	—	3·161	1	—
Mol. vol. .	81·184	38·042	119·226	82·616	36	119·626

Formation of Hydro-potassic Sulphate.

	SO^4H^2 +	KHO	Sum	SO^4KH +	H^2O	Sum
Mol. weight	98	56	—	136	18	—
Sp. gr. . .	1·842	2·100	—	2·163	1	—
Mol. vol. .	52·203	27·460	79·663	62·875	18	80·875

Formation of Ethyl Acetate.

	C^2H^6O +	$C^2H^4O^2$	Sum	$C^2H^3(C^2H^5)O^2$ +	H^2O	Sum
Mol. weight	46	60	—	88	18	—
Sp. gr. . .	0·809†	1·06	—	0·90	1	—
Mol. vol. .	57·5	56·5	114·0	97·8	18	115·8

H. L. Buff (*Ann. Ch. Pharm. Suppl.* iv. 129; *Jahresb.* 1866, p. 17) has carefully determined the specific gravities of a number of compounds into which the elements carbon, sulphur, and phosphorus may be supposed to enter with different atomicities or equivalent values. He finds that in saturated carbon-compounds, like propyl iodide, C^3H^7I, the atomic volume calculated according to Kopp's method (i. 445) agrees very nearly with the quotient obtained by dividing the molecular weight of the compound with its sp. gr. at the boiling point (calculated from the observed sp. gr. according to the known rate of expansion); but in unsaturated compounds—or such as, if regarded as saturated, may be supposed to contain bivalent carbon—like dichlorethylene, carbon dichloride, amylene, &c., the atomic volume calculated by Kopp's method differs from the quotient of the molecular weight by the sp. gr. (observed atomic volume) by quantities too great to be attributed to errors of observation; thus:

---

* At 15°. † At 0°.

Substance	Formula	Atomic volume at the boiling point		Difference	Atoms of bivalent carbon
		Observed	Calc.		
Dichlorethylene . .	$C^2H^2Cl^2$	79·9	78·6	+ 1·3	1
Carbon dichloride .	C^2Cl^4	115·4	113·2	+ 2·2	1
Ethyl cinnamate .	$C^{11}H^{12}O^2$	211·3	207·0	+ 4·3	1
Amylene	C^5H^{10}	111·24 – 112·47	110·0	+ 1·24 – 2·47	1
Diallyl	C^6H^{10}	126·7 – 127·0	121·0	+ 5·7 – 6·0	2
Valerylene	C^5H^8	103·27 – 104·88	99·0	+ 4·27 – 5·48	2

Hence Buff concludes that the atomic volume of bivalent carbon is greater than that of quadrivalent carbon.

Further, from the molecular volume of carbon bisulphide, CS.S, he calculates the atomic volume of sulphur within the radicle as 27·8 to 28·8; that of quadrivalent sulphur (in sulphurous acid) = 22·6, and that of sexvalent sulphur (in sulphuric anhydride) = 12, both for the intra-radicle position. The atomic volume of trivalent phosphorus he estimates at 25, that of quinquivalent phosphorus at 22. These results are regarded by Buff as leading to the conclusion that the chemical affinity of matter is in some way dependent upon the space which it occupies; and the density of a compound increases with the number of units of affinity with which its component elements enter into combination.

F. W. Clarke has directed attention to the relations between the atomic volumes of the elementary bodies in the liquid and solid states, showing that the atomic volumes of the elements in each equivalent group are in some cases exactly, in others approximately multiples of the lowest number in each group. In the group of the alkali-metals, for example, we have:

	Li	Na	K	Rb
Specific gravities	0·589	0·972	0·865	1·52
Atomic weights	7	23	39·1	85·4
Atomic volumes . . .	11·9	23·7	45·1	56·2

Here the atomic volumes are very nearly in the numbers 1 : 2 ; 4 : 5 (*Sill. Am. J.* [2] xlvii. 180, 308 ; *Zeitschr. f. Chem.* [2] v. 292, 359). The same paper contains observations on the relations between the atomic volumes of homologous and analogous compounds in the liquid state.

For Tschermak's speculations respecting atomic volumes, see *Ann. Ch. Pharm.* cxii. 129 ; cxiv. 25 ; *Jahresb.* 1859, p. 21 ; *Wien. Akad. Ber.* xli. 67 ; *Jahresb.* 1860 p. 20. For those of Groshans: *Ann. Ch. Pharm.* cxvi. 221 ; *N. Arch. ph. nat.* xvii. 5 ; xxiii. 73 ; *Jahresb.* 1860, p. 18 ; 1863, p. 31 ; 1865, p. 27. Of Kremers: *Pogg. Ann.* cxxii. 245.

ATOMICITY. This term is used to denote the equivalent value or combining capacity of an element, and, as explained in the article CLASSIFICATION (i. 1008), it is measured by the number of atoms of hydrogen or other monatomic or univalent element with which the element in question can combine.

Chlorine, which unites with only 1 atom of hydrogen, is monatomic, monadic, or univalent.

Oxygen, which combines with 2 atoms of hydrogen, is diatomic, dyadic, or bivalent.

Nitrogen, which combines with 3 atoms of hydrogen, is triatomic, triadic, or trivalent.

Carbon, which combines with 4 atoms of hydrogen, is tetratomic, tetradic, or quadrivalent.

When an element does not unite with hydrogen, as is the case with many of the metals, its atomicity may be measured by the number of atoms of chlorine, bromine, or iodine with which it can combine, since the atomicity of these elements is equal to that of hydrogen, and they may be substituted for it atom for atom; also by the number of univalent or monatomic radicles, such as CH^3, C^2H^5, OH, &c., that it can unite with, as in the case of lead, which is regarded as tetratomic because it forms with ethyl the compound $Pb(C^2H^5)^4$.

But the atomicity of an element cannot be estimated by the number of diatomic or polyatomic atoms that it may take up, for this number is indefinite. In fact, a diatomic element, like oxygen, may attach itself to another element or group of elements by one of its combining units, leaving the other free; and to this again another diatomic or other polyatomic element may be attached, and so on indefinitely. For example, we have the series of compounds

Potassium monosulphide	K—S—K
„ bisulphide	K—S—S—K
„ trisulphide	K—S—S—S—K, &c.

Moreover, we know that in by far the greater number of cases, polyatomic elements can unite with monatomic elements in more than one proportion; tin, for example, forms the chlorides $SnCl^2$, $SnCl^4$; antimony, the chlorides $SbCl^3$, $SbCl^5$.

Hence it is evident that the atomicity or combining capacity of elements is in most cases a variable quantity; and a comparison of all known cases of combining proportion shows that the atomicity or equivalent value of any given element in its several compounds always varies by two units, and that the elements may be divided in this respect into two classes, one of odd, the other of even equivalence, the former distinguished as perissads, the latter as artiads; e.g.,

Perissads: N, P, As, Sb, Au.
Artiads: O, S, Se, Te, Ba, Ca, Mg, Sn, Mo, W, &c.

In all cases of varying combining capacity, it has been usual to regard the highest value as representing the true atomicity of the element: thus tin, which forms the chlorides $SnCl^2$ and $SnCl^4$, is regarded as a tetrad; phosphorus, which forms the chlorides PCl^3 and PCl^5, as a pentad; nitrogen, which in the ammonium salts, NH^4Cl for example, unites with 5 monatomic atoms, also as a pentad.

In all these cases, the compounds in which the polyatomic element exhibits a degree of combining capacity below the maximum are unsaturated compounds, which, though capable of existing in the free state, are nevertheless ready to take up an additional number of atoms and pass to the saturated state, when placed under circumstances favourable to such combination. Thus stannous chloride, $SnCl^2$, readily takes up 2 at. Cl, and passes into stannic chloride, $SnCl^4$; in like manner PCl^3 is easily converted into PCl^5 or PCl^3O.

On the other hand, the least saturated compounds of such series are often in one respect more stable than the more saturated compounds. In the pentachloride of phosphorus, for example, the last two atoms of chlorine are less strongly attached to the phosphorus than the other three, so that the compound, under the influence of reducing agents, or even of heat, easily gives up these two atoms of chlorine, and passes to the trichloride; so likewise stannic chloride is reduced to stannous chloride; and in the ammoniacal salts, sal-ammoniac, NH^4Cl, for example, it is easy to remove HCl from the molecule (by the action of potash or other bases), and set free ammonia, NH^3; but to dissolve the union between the atom of nitrogen and the three atoms of hydrogen requires the exertion of a much greater amount of chemical force.

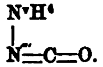
Hence it has been supposed that nitrogen and phosphorus are really triatomic elements, that is to say, incapable of uniting with more than 3 atoms of hydrogen or other monatomic elements, but that the compound thus formed can take up two other atoms as a molecule; that in sal-ammoniac, for example, the 4 at. H and 1 at. Cl are not all united directly to the nitrogen, but that the molecule NH^3 unites bodily with the molecule HCl, the union between them being, not atomic, but molecular, like that by which water of crystallisation is attached to a salt, or the molecular constituents of double chlorides are united together, as in $AgCl.KCl$; $PtCl^4.2KCl$, &c. This view receives some support from the fact that sal-ammoniac, NH^4Cl, exhibits an anomalous vapour-density, splitting up at high temperatures into NH^3 and HCl, and therefore exhibiting a condensation, not to two, but to four volumes. For a like reason, phosphorus pentachloride is supposed to be a compound of the saturated molecule PCl^3 with a molecule of chlorine, Cl^2; $SbCl^5$ as a compound of $SbCl^3$ with Cl^2; and iodine trichloride, ICl^3, a compound of ICl with Cl^2.

But this mode of viewing the constitution of such bodies is scarcely tenable. It is indeed impossible to regard phosphorus pentachloride, PCl^5, as consisting of two molecules, when its analogues PCl^3O and PCl^3S certainly consist of one only, these compounds exhibiting in the state of vapour the normal condensation to two volumes. Again, sal-ammoniac, NH^4Cl, which is isomorphous with potassium chloride, KCl, and, like the latter, unites to form a crystalline compound with platinic chloride, auric chloride, &c., must, like potassium chloride, be regarded as consisting, not of two molecules, but only of one. Lastly, if iodine trichloride were a compound of ICl and Cl^2, the last two atoms of chlorine ought to be easily separated from the third. But this is not the case. On the contrary, when this trichloride is treated with silver acetate, the three chlorine-atoms are removed at once as silver chloride, and Schützenberger's iodine-triacetate is formed:

$$ICl^3 + 3AgC^2H^3O^2 = 3AgCl + I(C^2H^3O^2)^3.$$

This reaction is a complete case of double decomposition, and shows that the compound ICl^3 forms one complete molecule, not two.

From all these facts we must conclude that there is no such thing as *absolute* atomicity or combining capacity, but that the combining capacity of any elementary atom depends upon the other atoms with which it comes in contact, or generally on the circumstances under which it is placed. Thus iodine is monatomic in the compounds IH, IAg, ICl, triatomic in ICl^3; phosphorus is triatomic in PCl^3 and PH^3, pentatomic in PCl^5; nitrogen is triatomic in NH^3, pentatomic in NH^4Cl and the other ammonium salts. Nitrogen indeed forms compounds in which it is at once triatomic and pentatomic, viz. in ammonium cyanate:

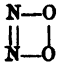


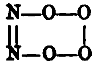
$$\begin{array}{l} N^vH^4 \\ | \\ \overset{'''}{N}\equiv C = O. \end{array}$$

In nearly all cases the combining capacity of an element in its several compounds varies, as already observed, by two units: thus iodine, gold, and thallium are monads and triads; phosphorus and its congeners are triads and pentads; silicon, titanium, selenium, tellurium, and tin are dyads and tetrads; sulphur and chromium are dyads, tetrads, and hexads. There is no well-established case of an element acting as a perissad in some cases, and as an artiad in others, excepting perhaps nitrogen, which in combination with oxygen exhibits the series

$$N^2O \qquad N''O \qquad \overset{'''}{N}{}^2O^3 \qquad N^{iv}O^2 \qquad \overset{v}{N}{}^2O^5.$$

Now in the first, third, and fifth of these compounds the atomicity of nitrogen follows the general law, but in the second and fourth this element appears as an artiad. It might be brought under the general law by doubling the formulæ, in which case the nitrogen would appear as a triad, the two oxides then being represented by the formulæ

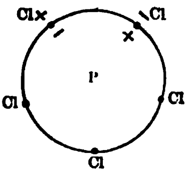




and this change would moreover bring the formulæ into accordance with the law of even numbers; but the density of the dioxide, which is a permanent uncondensable gas, shows that the simpler formula NO is in accordance with the general law of two-volume condensation. As to the tetroxide, it appears, from the determination of its vapour-density by Playfair and Wanklyn (iv. 76), to be capable of existing in the two polymeric modifications NO^2 and N^2O^4. Altogether the combining capacity of nitrogen exhibits peculiarities which are not yet satisfactorily explained.

The variation of combining capacity in an element by two or multiples of two is itself a phenomenon which has not yet received a perfectly satisfactory explanation. The point to be explained is, not that an element capable of taking up 5 atoms of chlorine, for example, should sometimes content itself with 3 atoms, and nevertheless form a compound possessed of considerable stability: for it is quite intelligible that an unsaturated compound, like PCl^3, may appear perfectly stable and quiescent until it is brought under particular conditions favourable to the saturation of its still uncombined units of affinity; indeed, were it not for the existence of such unsaturated atoms and molecules, there could for the most part be no such thing as direct chemical combination, since saturated molecules cannot take up new elements except by substitution.

But it does not appear from this why the variation of atomicity should always take place by pairs of units. Frankland endeavours to account for this circumstance by supposing that in an atom of any polyatomic element the points of attachment by which the atom unites itself to other atoms are capable of neutralising one another more or less completely, like contiguous electric or magnetic poles of opposite name. Granting this, we may suppose that when 3 poles in the atom of a pentatomic element, phosphorus for example, have been neutralised by combination with 3 atoms of a monatomic element, such as chlorine, the remaining two may still be free, but in opposite polar (? electrical) states, so that the molecule PCl^3 may appear perfectly neutral and stable. But now let a molecule of chlorine, $\overset{-}{Cl}\overset{+}{Cl}$,

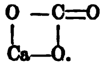


having its two component atoms in opposite polar states, approach this molecule. The two atoms will then place themselves so that the opposite poles of the chlorine and the phosphorus may come opposite to one another, and then combination will take place, the trichloride being converted into the pentachloride. In like manner we may suppose that the atom of any polyatomic element, tin for example, may contain two such pairs of opposite poles, and that when brought in contact with chlorine it may take up, first one molecule of that element in the manner just described, and then another, a pair of its poles being brought into activity at each step. This mode of viewing the process may afford some explanation of the fact that change of atomicity in elements almost always takes place by pairs of units.

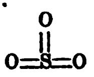
The same hypothesis may account for the circumstance that a molecule of a perissad element always contains an even number, generally a pair of atoms, the molecule of hydrogen, for example, consisting of HH, that of nitrogen of NN, &c.; for as the opposite poles of such an atom neutralise one another in pairs, there must always be one left uncombined, and neutralisable by union with a pole of opposite name belonging to another atom. Artiad elements, on the other hand, may also unite in this manner—the molecule of oxygen, for example, being supposed to consist of two atoms, OO; but since each of their poles may be neutralised by a pole of opposite name, they may also exist in the free state as single atoms; in fact, the vapour-densities of mercury, cadmium, and zinc show that the atoms of these elements in the free state exist singly and not in pairs.

Further, it is necessary to remark that saturation is not necessarily perfect, even when all the combining capacities of the elements in a molecule appear to be satisfied. There are indeed but few compounds that appear perfectly saturated, and therefore incapable of combining directly with any other atoms or molecules. The paraffins C^nH^{2n+2} exhibit this character, being incapable of direct combination, and being modified only by substitution; but platinic chloride, $PtCl^4$, which is also generally regarded as a saturated molecule, cannot be so in the same degree as the compound CH^4 or CCl^4, inasmuch as it can form definite crystalline compounds with various other metallic chlorides. In such double chlorides, indeed, the combination is commonly said to be molecular, rather than atomic; between the molecules as wholes, rather than between the individual atoms; but molecules could scarcely exhibit any tendency to combine if the combining tendencies or opposite polarities of their component atoms were completely neutralised. At all events, the state of a perfectly neutral molecule, like CH^4, must be different from that of one which, like $PtCl^4$, still exhibits a tendency to take up additional elements and form definite compounds therewith. The same must be the case with all salts and other compounds which can take up water of crystallisation. Their union with this water is attended with evolution of heat, just like combination between atoms; in such molecules, therefore, the combining tendencies of the component atoms cannot be supposed to be perfectly neutralised.

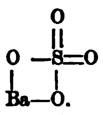
In some cases, however, combination between two saturated compounds may take place in consequence of a different arrangement of the atoms, and a difference in the manner in which they are linked together; thus carbon dioxide, $O{=}C{=}O$, and lime, $Ca{=}O$, are both saturated compounds; nevertheless they can combine directly under certain circumstances and form calcium carbonate:

$O{=}C{=}O$ and $Ca{=}O$ form 

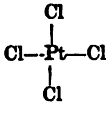
In like manner, sulphuric oxide, SO^3, and baryta, BaO, unite at high temperatures to form barium sulphate:



$$\begin{array}{c} O \\ \| \\ O{=}S{=}O \end{array}$$

and $Ba{=}O$ form 

But this kind of combination can take place only when both molecules consist wholly of polyatomic elements. In the case of combination between chlorides, on the contrary, such as platinic chloride and hydrogen chloride,



$$\begin{array}{c} Cl \\ | \\ Cl{-}Pt{-}Cl \\ | \\ Cl \end{array}$$

and $H{-}Cl$,

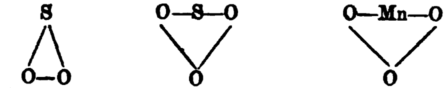
there are no uncombined units of affinity to lay hold of. It is conceivable, however, that the polarities of this atom of platinum may be neutralised by the opposite polarities of the chlorine-atoms so far as not to be further excited by the comparatively feeble polarities of the two atoms composing another chlorine molecule, $\overset{+}{\mathrm{Cl}}\ \overset{-}{\mathrm{Cl}}$, but may yet be roused into action by the stronger polarities of such a molecule as potassium chloride, $\overset{+}{\mathrm{K}}\ \overset{-}{\mathrm{Cl}}$, and in this manner combination may take place between the two molecules.

Allusion has already been made to the power of polyatomic elements to accumulate in compounds. Two diatomic elements, for example, may unite together so as to completely neutralise all their units of affinity, as in the compounds $\mathrm{Ba{=}O}$; $\mathrm{Pb{=}S}$. But they may also unite so as each to leave a unity of atomicity free; in such cases other elements may enter the combination to satisfy the uncombined units; as in the following examples:

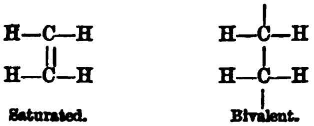
$\mathrm{H{-}O{-}O{-}H}$ Hydrogen dioxide. $\mathrm{H{-}O{-}O{-}Cl}$ Chlorous acid. $\mathrm{Cl{-}O{-}O{-}O{-}Cl}$ Chlorous oxide or anhydride.

$\mathrm{H{-}O{-}O{-}O{-}O{-}Cl}$ Perchloric acid.

In these examples we see that a chain of any number of oxygen-atoms, united together by one unit of atomicity belonging to each, must always leave an uncombined unit at each end, which may be neutralised or satisfied by a monatomic atom, such as hydrogen or chlorine. A chain of diatomic or other polyatomic atoms thus connected together, and having uncombined units at each end, is called an open chain. It is possible, however, that the atoms of the extremities may unite between themselves by their uncombined units, and thus form a closed chain; thus:


Sulphurous anhydride. Sulphuric anhydride. Manganic anhydride.

The equivalent or combining value of any group of atoms must evidently depend partly upon the atomicity of the individual elements, partly on the manner in which they are linked together: thus the group C^2H^4 may be saturated or bivalent, accordingly as the two carbon-atoms are grouped by one or by two of their units of affinity:

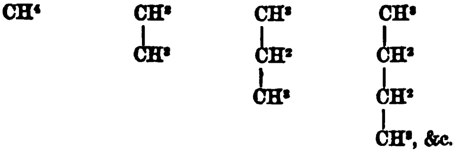

$$\begin{array}{c} \mathrm{H{-}C{-}H} \\ \| \\ \mathrm{H{-}C{-}H} \end{array} \qquad \begin{array}{c} | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \end{array}$$

Saturated. Bivalent.

Any given group of atoms will evidently exhibit its maximum atomicity or combining capacity, or will have the greatest possible number of combining units free, when all the polyatomic atoms are linked together by one unit of affinity only. In such a case it has been shown in the article CLASSIFICATION (i. 1013) that in a group of *n* polyatomic atoms, A'', A''', A^{iv} . . . , thus united, the maximum atomicity is represented by the formula

$$A'' + A''' + A^{iv} \ldots - 2(n - 1).$$

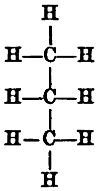
A very important case of this law is that of a number of carbon-atoms united together, as in marsh gas and its homologues; thus:

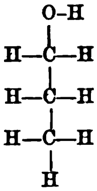

$$\mathrm{CH^4} \qquad \begin{array}{c} \mathrm{CH^3} \\ | \\ \mathrm{CH^3} \end{array} \qquad \begin{array}{c} \mathrm{CH^3} \\ | \\ \mathrm{CH^2} \\ | \\ \mathrm{CH^3} \end{array} \qquad \begin{array}{c} \mathrm{CH^3} \\ | \\ \mathrm{CH^2} \\ | \\ \mathrm{CH^2} \\ | \\ \mathrm{CH^3} \end{array}, \text{ \&c.,}$$

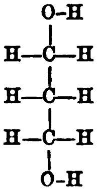
in which the group of *n* tetrad atoms exhibits an atomicity denoted by $4n - 2(n - 1) = 2n + 2$. A group of two carbon-atoms will therefore take up 6 atoms of hydrogen; a group of three carbon-atoms will take up 8 hydrogen-atoms, and so forth, each hydrocarbon of the series differing from the preceding by CH^2.

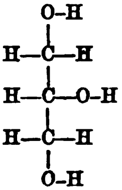
When any number of hydrogen-atoms in a compound is replaced by an equal number of atoms of chlorine or other monatomic element, or by an equivalent number of multivalent atoms, or univalent and multivalent atoms combined, it is clear that the combining capacity of the group will remain the same as before. Chloroform, $CHCl^3$, for example, derived from marsh gas by substitution of Cl^3 for H^3, is a saturated compound like marsh gas itself; so likewise is aldehyde, C^2H^4O, derived from ethane, C^2H^6, by substitution of O'' for H^2; but dichlorethylene, $C^2H^2Cl^2$, is bivalent, like ethylene, C^2H^4, itself.

Suppose now an atom of hydrogen in any group to be replaced by oxygen, as when the compound is subjected to the action of oxidising agents. In this case the diatomic oxygen which enters the group attaches itself thereto by one of its units of affinity, leaving the other free, and capable therefore of retaining in the group the hydrogen which it has displaced. The final result is the replacement of an atom of hydrogen by the univalent group or radicle, hydroxyl, OH: thus in propane or propyl hydride, C^3H^8, we may replace H by OH, yielding propyl alcohol, $C^3H^7(OH)$; a second similar substitution produces propylene alcohol, or propylic glycol, $C^3H^6(OH)^2$; and a third produces propenyl alcohol or glycerin, $C^3H^5(OH)^3$:


Propane.

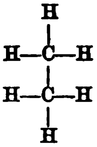

Propyl alcohol.

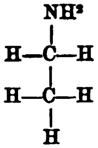

Propylene glycol.

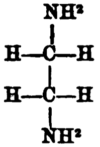

Glycerin.

The result of these substitutions of OH for H is evidently an addition of one atom of oxygen to the molecule at each successive step.

In like manner, nitrogen (trivalent) taking the place of an atom of hydrogen may bring with it two other hydrogen-atoms to complete the saturation, as in the derivation of ethylamine, C^2H^7N, and ethylene-diamine, $C^2H^8N^2$, from ethane, C^2H^6.


Ethane.


Ethylamine.


Ethylene-diamine.

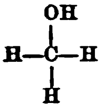
The result is the addition of NH to the molecule at each step.

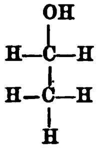
Quinquivalent nitrogen substituted for hydrogen brings with it 4 atoms of hydrogen, as in the formation of ammonium-salts from their respective acids, the result being equivalent to the addition of NH^3 at each successive step.

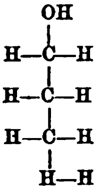
Instead of 2 or 4 at. hydrogen, nitrogen, accordingly as it enters a molecule in its trivalent or quinquivalent capacity, may bring with it 1 or 2 atoms of oxygen, the result being the replacement of the hydrogen by nitrosyl, NO, in the one case, and of nitryl, NO^2, in the other: e.g.,

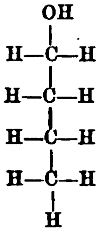
C^6H^7N	$C^6H^6(NO)N$	$C^6H^6(NO^2)N$
Aniline.	Nitrosaniline.	Nitraniline.

Carbon, which is tetratomic, entering in like manner into a molecule, takes with it 3 atoms of hydrogen, and thereby increases the molecule by the addition of CH^2 at each successive step, the result being, as is well known, the formation of homologous series: thus in the series of alcohols $C^nH^{2n+2}O$:

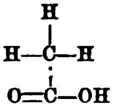

Methyl alcohol.

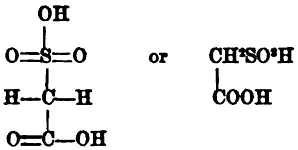

Ethyl alcohol.


Propyl alcohol.


Butyl alcohol.

Sulphur, regarded as sexvalent, may take with it into combination the quinquivalent group $O''O''(OH)$, the result being the substitution of the univalent radicle SO^3H for H, or the addition of SO^3 to the original molecule. The compound thus formed is usually a **sulpho-acid**, as sulphacetic acid, $C^2H^4O^2.SO^3$, from acetic acid:

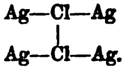

Acetic acid.


Sulphacetic acid.

Classification of Elementary Bodies according to their Atomicities.

This subject has been discussed in the article CLASSIFICATION, by Prof. G. C. Foster, and in that on METALS, ATOMIC WEIGHTS AND CLASSIFICATION OF, by Dr. Odling; but a few additional observations are required to bring it into accordance with the results of recent researches. A table of the elementary bodies classified according to the views of their atomicities or combining capacities, now most generally received, will be found at the end of this article. It must be distinctly understood, however, that the atomicities there assigned to the several elements are by no means absolute, but only such as these elements exhibit in their more important compounds.

1. *Monads.*—The atomicity of **hydrogen**, as exhibited in the single compound which it forms with chlorine, is assumed as the standard of atomicity, equivalent value, or combining capacity. Estimated by this standard, **silver** appears to be always univalent; but the other elements usually classed as monads, though certainly univalent in most of their compounds, nevertheless appear to be also capable of exhibiting higher equivalent values. **Chlorine** is univalent in argentic chloride, $AgCl$; but in argentous chloride, Ag^2Cl, or rather Ag^4Cl^2, it appears to be trivalent, the constitutional formula of that compound being



$$\begin{matrix}Ag—Cl—Ag\\ |\\ Ag—Cl—Ag.\end{matrix}$$

Bromine must also be regarded as trivalent in the corresponding compound Ag^4Br^2; and **iodine**, because it forms a trichloride, ICl^3. Chlorine and iodine might even be regarded as septivalent, viz. in perchloric acid, $Cl^{vii}\left\{\begin{matrix}O''^3\\OH\end{matrix}\right.$, periodic acid, $I^{vii}\left\{\begin{matrix}O''^3\\OH\end{matrix}\right.$, and the corresponding anhydride, I^2O^7; but these oxygen-acids of chlorine and iodine may also be represented by different formulæ, in which the oxygen-atoms are linked together, and the chlorine and iodine are univalent (p. 241). **Fluorine** is most probably a monad, but still there are some reasons for regarding it as a dyad analogous to oxygen (ii. 272). **Sodium** and the other alkali-metals are univalent in most of their compounds; but Wanklyn has lately shown that sodium can also act as a trivalent and as a septivalent element. The crystals commonly called sodium ethylate, and represented by the formula C^2H^5NaO, have, according to Wanklyn, a more complex constitution, consisting, when dried at 100°, of

$$\left.\begin{array}{r}\left.\begin{array}{r}C^2H^5O\\H\end{array}\right\}\\\left.\begin{array}{r}C^2H^5O\\H\end{array}\right\}\\\left.\begin{array}{r}C^2H^5O\\H\end{array}\right\}\\C^2H^5O\end{array}\right\}Na^{vii}.$$

When kept for a long time at 200°, they give off 4 molecules of alcohol, $(C^2H^5O)H$, leaving sodium ethylate or hydrate of ethylene-sodium:

$$\left.\begin{array}{r}(C^2H^4)''\\HO\end{array}\right\}Na'''.$$

Potassium acts upon alcohol in the same manner as sodium, and will probably be found to yield analogous products.

2. *Dyads.*—The non-metallic elements, oxygen, sulphur, selenium, and tellurium, must be regarded as dyads, if we look only to their hydrogen-compounds; but the three last-mentioned elements form compounds into which they appear to enter as tetrads and hexads; and if argentous oxide be correctly represented by the formula Ag^4O, even oxygen must be regarded as a tetrad.

The chemical relations of the metals now regarded as dyads are fully discussed in Dr. Odling's article above referred to.

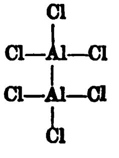
3. The *triad* elements are boron, thallium, and gold. Of the trivalence of boron there is no question. Thallium and gold are both univalent and trivalent, the mono-compounds of the former and the tri-compounds of the latter being the most stable. Gold may, however, be regarded as trivalent also in the aurous compounds if we double their formulæ: thus $Au^2Cl^2 = \begin{array}{l}Au—Cl\\ \| \\Au—Cl\end{array}$. Thallium, as a univalent element, exhibits a very close analogy to the alkali-metals (v. 753).

4. *Tetrads.*—Carbon is quadrivalent in all its compounds, except the monoxide $C{=}O$, in which it is bivalent; but this is an unsaturated compound, ready to take up an additional atom of oxygen or two atoms of chlorine.

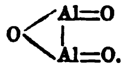
Silicon, titanium, and tin are bi- and quadrivalent.

Zirconium forms a tetrachloride, $ZrCl^4$, and a dioxide, ZrO^2, and is indeed quadrivalent in all its compounds.

Aluminium forms but one class of compounds, in which it is apparently trivalent, the chloride being represented by the formula $AlCl^3$, the methide and ethide by $Al(CH^3)^3$ and $Al(C^2H^5)^3$, and the oxide by Al^2O^3. This view is in accordance with the vapour-densities of the ethide and methide at high temperatures (iii. 983). On the other hand, the vapour-density of the chloride, as determined by Deville, points to the formula Al^2Cl^6, and similarly those of the methide and ethide near their boiling points accord more nearly with the double formulæ $Al^2(CH^3)^6$ and $Al^2(C^2H^5)^6$ than with the simpler formulæ above given. If these double formulæ are correct, aluminium may be regarded as quadrivalent, its chloride and oxide being represented by the formulæ



and



This latter view is corroborated by the isomorphism between alumina and ferric oxide and their corresponding salts.

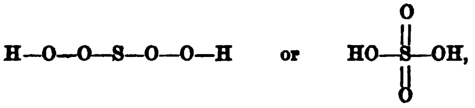
Cerium, uranium, cobalt, and nickel are bivalent and quadrivalent. They all form dichlorides. Of cerium a native trifluoride Ce^2F^6 is known, analogous in composition to the chloride of aluminium. No trichloride of uranium is known; but the oxychloride, $U^2O^2Cl^2$, derived from the trichloride by substitution of O^2 for Cl^4, is a well-known compound. Cobalt forms a trichloride, Co^2Cl^6. Of nickel only the dichloride, $NiCl^2$, has been obtained; but the sesquioxide, Ni^2O^3, is known, analogous to cobaltic oxide, and from the close resemblance of nickel to cobalt in all its chemical relations, it evidently belongs to the same class. All the four metals included in this paragraph are also analogous in many respects to iron, manganese, and chromium, and might accordingly be regarded as hexads; but, as no compounds are actually known in which they appear to be sexvalent, it is best to regard them as tetrads.

Lead is bivalent in the only chloride which it forms, viz. $PbCl^2$, and in its basic oxide, PbO; quadrivalent in plumbic ethide, $Pb(C^2H^5)^4$, and in the dioxide, PbO^2.

Platinum, palladium, iridium, and **rhodium** are bivalent and quadrivalent. **Platinum** and **palladium** form dichlorides and tetrachlorides, and corresponding oxides. **Iridium** forms a dichloride, a tetrachloride, and an intermediate chloride, Ir^2Cl^6, which may be regarded as analogous in composition to ferric chloride and aluminium chloride, that is as containing quadrivalent iridium. **Rhodium** forms only a dichloride, $RhCl^2$, and a trichloride, Rh^2Cl^6. These two metals also form oxides analogous in composition to the chlorides, and yielding corresponding salts with acids, and likewise higher oxides, viz. IrO^3 and RhO^3.

5. *Pentads.*—Among these elements, **nitrogen, phosphorus, arsenic, antimony,** and **vanadium** form one natural group; **tantalum** and **niobium** another. The reasons for regarding **nitrogen** as quinquivalent as well as trivalent have already been given (p. 238). **Phosphorus** and **antimony** form trichlorides and pentachlorides, with corresponding oxides, oxy-salts, and organo-metallic bodies. **Arsenic** forms only a trichloride, but its oxygen-compounds, sulphur-compounds, and organo-metallic compounds are analogous to those of phosphorus. **Bismuth** forms a trichloride and a dichloride, Bi^2Cl^4 or $\begin{array}{c}BiCl^2\\ |\\ BiCl^2\end{array}$, in both of which it is trivalent; also corresponding organo-metallic compounds and oxides. It also forms a pentoxide, with corresponding salts, whence, and from its analogy with antimony, it is regarded as a pentad. **Vanadium** was formerly regarded as a hexad; but Roscoe has lately shown that it is a pentad (v. 984). **Tantalum** and **niobium** were formerly regarded as tetrads; but the recent experiments of Marignac have shown that they are pentads (iv. 785; v. 662).

6. *Hexads.*—**Sulphur, selenium,** and **tellurium** are bivalent in their hydrogen-compounds, quadrivalent in their chlorides, those of selenium and tellurium being definite and stable compounds in the free state, whereas the tetrachloride of sulphur is known only in combination with metallic chlorides (v. 535). In sulphurous triethiodide, $S\left\{\begin{array}{l}(C^2H^5)^3\\ I\end{array}\right.$ (v. 881), sulphur is undoubtedly quadrivalent, and in sulphuric ethylene-diethyl-bromide, $S\left\{\begin{array}{l}(C^2H^4)''\\ (C^2H^5)^2\\ Br^2\end{array}\right.$, it appears to be sexvalent. The same degree of atomicity is likewise exhibited by sulphur in the sulphates. Sulphuric acid or hydrogen sulphate might indeed be represented by either of the formulæ



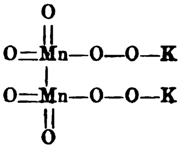
$$H—O—O—S—O—O—H \quad \text{or} \quad HO—\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}—OH,$$

in the former of which the sulphur is bivalent, while in the latter it is sexvalent. But the stability of the sulphates is rather in favour of the latter view, inasmuch as compounds in which oxygen is directly united with oxygen, as in the first formula, are usually rather unstable. Moreover, the sulphates are isomorphous with the chromates, and should therefore be represented by similar formulæ; now chromium is undoubtedly a hexad. **Selenium** and **tellurium**, which are analogous to sulphur in nearly every respect, and especially in the constitution of their highest oxygen-acids, must in like manner be regarded as hexads.

Chromium forms a hexfluoride, CrF^6, to which there corresponds the trioxide or chromic anhydride, CrO^3, with the corresponding salts; potassium monochromate, K^2CrO^4, for example, may be represented by a formula exactly similar to the second of the two above given for hydrogen sulphate. Chromium also forms the chromous salts, in which it is bivalent, e.g. $CrCl^2$, and the chromic salts, e.g. Cr^2Cl^6, in which it is quadrivalent. (See CHROMIUM.)

Iron exhibits combining capacities exactly analogous to those of chromium. In the ferrous compounds, as $FeCl^2$, it is bivalent; in the ferric compounds, quadrivalent, ferric chloride being represented, like aluminium chloride, by the formula $\begin{array}{c}FeCl^3\\ |\\ FeCl^3\end{array}$. In the ferrates, supposing their constitution to be well established, iron must be regarded as sexvalent, the formulæ of those salts being analogous to those of the sulphates and chromates; potassium ferrate, for example, being represented by the formula $\mathrm{Fe^{vi}K^2O^4}$ or $\mathrm{Fe^{vi}O^2(OK)^2}$.

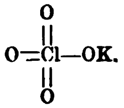
Precisely similar observations may be applied to **manganese** in the manganous and manganic salts, and in the manganates respectively. The manganates are isomorphous with the chromates, which corroborates the supposition that the manganese in these salts is sexvalent. Manganese however forms a class of still more highly oxidised salts, viz. the permanganates, as $\mathrm{MnKO^4}$ or $\mathrm{Mn^{vii}O^3(OK)}$, to which there are said also to be a corresponding chloride, $\mathrm{MnCl^7}$, and fluoride, $\mathrm{MnF^7}$ (iii. 805, 808). This would seem to show that manganese can also be septivalent, a fact not in accordance with the general law that the variation of combining capacity in any element takes place by successive increments of two units. But the so-called heptachloride appears from H. Rose's experiments to be really an oxychloride, $\mathrm{MnO^2Cl^2}$, analogous to chromic oxychloride; and the so-called heptafluoride has probably a similar composition, the manganese being sexvalent in both compounds. The constitution of the permanganates may also be represented by a formula in which manganese is sexvalent. The potassium salt, for example, may be represented as $\mathrm{Mn^2K^2O^8}$, or



$$\begin{array}{c} \mathrm{O} \\ \| \\ \mathrm{O{=}Mn{-}O{-}O{-}K} \\ | \\ \mathrm{O{=}Mn{-}O{-}O{-}K} \\ \| \\ \mathrm{O} \end{array}$$

It is true that the permanganates are isomorphous with the perchlorates, in which chlorine must be regarded either as univalent or septivalent; thus for the potassium salt:

$$\mathrm{Cl{-}O{-}O{-}O{-}O{-}K} \quad \text{or}$$



$$\begin{array}{c} \mathrm{O} \\ \| \\ \mathrm{O{=}Cl{-}OK.} \\ \| \\ \mathrm{O} \end{array}$$

But although isomorphous compounds very frequently, and perhaps in most cases, contain polyatomic elements of equal combining capacity, still this rule is not invariable: Marignac, for example, has shown that the fluotantalates and fluoniobates are isomorphous with the fluosilicates, fluotitanates, and fluostannates; and nevertheless tantalum and niobium are pentads, whereas silicon, titanium, and zirconium are tetrads. The balance of evidence is therefore in favour of regarding manganese in the permanganates as a hexad.

Molybdenum forms a hexfluoride known in combination, though not in the free state; also a tetrachloride and dichloride, together with corresponding oxides.

Tungsten forms a hexchloride and tetrachloride, with corresponding oxides.

Ruthenium and **osmium** form chlorides analogous to those of iridium, e.g. $\mathrm{RuCl^2}$, $\mathrm{Ru^2Cl^6}$, and $\mathrm{RuCl^4}$, also hexchlorides $\mathrm{RuCl^6}$ and $\mathrm{OsCl^6}$, known however only in combination. The two metals also form oxides analogous to these several chlorides, and likewise higher oxides, viz. $\mathrm{RuO^4}$ and $\mathrm{OsO^4}$. From this it might be inferred that ruthenium and osmium are octads; but, as already observed, the atomicity of an element cannot safely be inferred from the number of atoms of oxygen or any other polyatomic element with which it may unite.

The following table exhibits a classification of the elementary bodies according to the principles above explained, together with their atomic weights according to the most recent determinations. The atomicity assigned to each element is the highest that it exhibits in its most important and best defined compounds. The elements are further divided by horizontal lines into groups consisting of elements closely related in their chemical characters; and in each of these groups the elements are arranged according to their atomic weights, beginning with the lowest.

TABLE OF THE ELEMENTARY BODIES, WITH THEIR ATOMIC WEIGHTS.

Elementary Bodies	Atomic Weights	Elementary Bodies	Atomic Weights
MONADS:		TETRADS, *continued*:	
Hydrogen	1	Aluminium	27·4
Fluorine	19	Zirconium	89·6
Chlorine	35·5	Cobalt	58·8
Bromine	80	Nickel	58·8
Iodine	127	Cerium	92
Lithium	7	Indium	198
Sodium	23	Uranium	120
Potassium	39·1	Lead	207
Rubidium	85·4	Rhodium	104·4
Cæsium	133	Palladium	106
Silver	108	Platinum	197·4
DYADS:		Iridium	198
Oxygen	16	PENTADS:	
Calcium	40	Nitrogen	14
Strontium	87·6	Phosphorus	31
Barium	137	Vanadium †	51·2
Glucinum	9·4	Arsenic	75
Thorinum *	57·9	Antimony	122
Yttrium	61·6	Bismuth	210
Lanthanum	93·6	Niobium ‡	94
Didymium	95	Tantalum §	182
Erbium	112·6	HEXADS:	
Magnesium	24	Sulphur	32
Zinc	65·2	Selenium	79·4
Cadmium	112	Tellurium	128
Copper	63·4	Chromium	52·2
Mercury	200	Manganese	55
TRIADS:		Iron	56
Boron	11	Molybdenum	96
Gold	197	Tungsten	184
Thallium	204	Ruthenium	104·4
TETRADS:		Osmium	199·2
Carbon	12		
Silicon	28		
Titanium	50		
Tin	118		

ATRACTYLIC ACID. $C^{30}H^{54}O^{23}.S^2O^6$? ‖ (E. Lefranc, *Bull. Soc. Chim.* [2] xi. 499).—The potassium salt of this acid exists in the root of *Atractylis gummifera*, and may be extracted therefrom by exhaustion with boiling alcohol of 56 to 75 p. c., from which it crystallises on cooling. By converting it into a lead-salt, and decomposing the latter with hydrogen sulphide, the *hydrogen salt* or *acid* is obtained. It is very soluble in water, inodorous, with a sour, styptic, and bitter taste. Its concentrated solution is easily decomposed by heat. The acid has not been obtained in the solid state.

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* Thorina = Th.O (see vol. v. p. 786).

† Vanadic oxide = V^2O^5 (Roscoe, v. 986).

‡ Niobic oxide = Nb^2O^5 (Marignac, iv. 784).

§ Tantalic oxide = Ta^2O^5 (Marignac, v. 664).

‖ Lefranc gives the formula $S^4O^{12}.C^{60}H^{53}O^{36}.3HO$, which is improbable, on account of the odd number of hydrogen-atoms.

Atractylic acid is tribasic, forming salts containing 1, 2, and 3 atoms of metal. They are crystallisable, soluble in water and in weak alcohol, much more soluble at high than at ordinary temperatures.

The *triargentic salt* forms a nacreous mass of microscopic crystals: it is very unstable. The *tribaric salt* crystallises in hexagonal dodecahedrons, and in six-sided prisms with pyramidal summits. The *potassio-calcic salt* $Ca''K^4(C^{30}H^{51}O^{23}.S^2O^6)^2$ is obtained by decomposing the native potassium salt with calcium carbonate, and adding alcohol, as a white granular crystalline precipitate. There are two *potassio-baric salts*, $Ba''K^4(C^{30}H^{51}O^{23}.S^2O^6)^2$ and $Ba''K.C^{30}H^{51}O^{3}.S^2O^6$, obtained by decomposing the preceding salt with barium chloride in different proportions.

Bimetallic Salts.—The native *potassium salt* $K^2H.C^{30}H^{51}O^{23}.S^2O^6$ is colourless, inodorous, bitter, and crystallises in prismatic needles. It is lævogyrate, with a rotatory power of 5·77°; at 100° it swells up, blackens, and gives off valeric acid. By calcination it leaves a residue of neutral potassium sulphate amounting to 20 p. c. Its solution is not precipitated by barium-salts till it has been decomposed by an acid, in which case it yields sulphuric acid, valeric acid, glucose, and a resinous matter. Hence atractylic acid appears to be a conjugated sulpho-acid of complex constitution; it is remarkable as being the first-known example of such an acid existing ready-formed in the vegetable organism. The corresponding *barium salt*, $Ba''H.C^{30}H^{51}O^{23}S^2O^6$, crystallises in very light silky tufts. The *zinc salt* $Zn''H.C^{30}H^{51}O^{23}S^2O^6$ resembles it. The *diargentic salt* is white, nacreous, and very unstable.

The *monometallic actractylates* are prepared by means of the salt $Ba''K.C^{30}H^{51}O^{23}.S^2O^6$, this salt being decomposed by a quantity of sulphuric acid just sufficient to precipitate the barium. They cannot be obtained in the solid state, on account of their tendency to decompose into the free acid (hydrogen salt) and a bimetallic salt.

ATROPIC ACID. See the next article.

ATROPINE. According to Gulielmo (*Zeitschr. anal. Chem.* ii. 404), this base, in quantity not exceeding $\frac{1}{40}$ to $\frac{1}{50}$ of a grain, may be detected by the intense odour, resembling that of the flowers of oranges and wild plums, which is evolved on heating it with a few drops of strong sulphuric acid till it turns brown, and then adding a few drops of water. When very carefully sublimed in the manner described under ALKALOÏDS (p. 87), it condenses in transparent drops, which if left for 24 hours in contact with hydrochloric acid, are converted into distinct octohedrons (Helwig, *ibid.* iii. 43). With *phosphomolybdic acid* it forms a yellow precipitate which dissolves in ammonia, forming a blue solution becoming colourless on boiling (J. Trupp, *Jahresb.* 1863, p. 702). It is decomposed by boiling with dilute *sulphuric acid* and *potassium bichromate*, with formation of benzoic acid; and the solution, which has become green, gives off, when supersaturated with potash, a volatile base smelling like herring-pickle. An odour of benzoic acid is likewise evolved when atropine burns in contact with the air (H. Ludwig, *Arch. Pharm.* [2] cvii. 129).

Atropine sulphate may be obtained in crystals by carefully neutralising a solution of the base in 8 grms. absolute alcohol with a mixture of sulphuric acid (0·5 grms.) and absolute alcohol, and leaving the solution to evaporate. The salt, which crystallises in stellate groups of needles having a mother-of-pearl lustre, is soluble in water and in alcohol, but not in ether or chloroform (Laveau, *J. Pharm.* [3] xliv. 132).

Ethyl-atropium iodide, $C^{19}H^{28}NO^3I$ or $C^{17}H^{18}(C^2H^5)NO^3I$, is formed, as a crystalline precipitate, on heating an ethereo-alcoholic solution of atropine with ethyl-iodide over the water-bath. The corresponding *chloride*, obtained by treating the iodide with silver-chloride, forms with platinic chloride the double salt $2C^{19}H^{28}NO^3Cl.PtCl^4$, which crystallises in orange-coloured laminæ. The iodide treated with silver oxide yields an easily soluble, uncrystallisable base, which, by renewed treatment with ethyl-iodide, is converted into an iodine-compound, appearing, from the analysis of the corresponding platinum salt, to consist of hydriodide of tropine (v. 895), resulting from a further decomposition (Lossen).

Acids produced by decomposition of Atropine.

According to Kraut (v. 895), atropine is resolved by the action of baryta-water at 58°, or of hydrochloric acid, into tropine and atropic acid:

$$\underset{\text{Atropine.}}{C^{17}H^{23}NO^{3}} = \underset{\text{Tropine.}}{C^{8}H^{15}NO} + \underset{\text{Atropic acid.}}{C^{9}H^{8}O^{2}}$$

According to Lossen (*Ann. Ch. Pharm.* cxxxviii. 230), atropine is resolved, either by baryta-water or by hydrochloric acid, into tropine and tropic acid, $C^9H^{10}O^3$, containing 1 mol. H^2O more than atropic acid:

$$C^{17}H^{23}NO^{3} + H^{2}O = C^{8}H^{15}NO + C^{9}H^{10}O^{3};$$

and the tropic acid, by the further action of these reagents, is converted, with elimination of water, into two isomeric acids, which he designates as atropic and isatropic acids. These acids are isolated as follows: Atropine is heated with fuming hydrochloric acid to 120°–130° for several hours, whereby a semifluid layer is produced containing the acids (and increasing on dilution with water). The dilute liquid contains, besides tropine hydrochloride, nothing but tropic acid, which may be extracted by ether. The semifluid mixture treated with dilute sodium carbonate yields a solution from which, by saturation with hydrochloric acid, isatropic acid, nearly insoluble in water, is separated, while tropic acid remains in solution, together with atropic acid, which is present in small quantity only. Both these acids are extracted from the solution by ether, the ether is evaporated, and the residue is treated with benzol, which dissolves scarcely anything but the atropic acid; the two acids are then purified by recrystallisation from boiling water. The isatropic acid precipitated by hydrochloric acid generally contains also a semifluid acid, easily soluble in alcohol and ether, but not yet further examined (Lossen; see also Kraut, *Ann. Ch. Pharm.* cxlviii. 236).

Tropic Acid, $C^9H^{10}O^3$, separates from hot saturated aqueous solutions in slender prismatic crystals grouped in hemispherical cauliflower-like masses; it is soluble in alcohol, in ether, and in 40 pts. of water at 14·5°; has a slightly sour taste, melts at 117°–118°, and does not volatilise without decomposition. The *calcium salt* $C^{18}H^{18}CaO^6.4H^2O$ crystallises in the form described by Kraut for calcium atropate (*infra*). According to recent observations by Kraut (*loc. cit.*), this salt crystallises in rhomboïdal plates of 100° 39′, with 4 mols. of water; it may also be obtained anhydrous in needles. It does not diminish sensibly in weight when heated to 200° for two or three hours in an atmosphere of hydrogen, but when exposed to the air at 100° its composition slowly approaches that of the atropate. At 220° it decomposes, giving off oily drops having the odour of bitter almonds, and leaving carbonate, atropate, and isatropate of calcium. The *silver salt* $C^9H^9AgO^3$, obtained by precipitation, crystallises from hot water and decomposes at 110°–120° (Lossen).

Atropic Acid, $C^9H^8O^2$, isomeric with cinnamic acid, is produced by heating tropic acid with concentrated baryta-water to 130° for several hours (Lossen). For Kraut's method of preparing it directly from atropine, see v. 895. This acid crystallises from aqueous solution in needles having the odour of benzoic acid, and from alcohol in monoclinic prisms exhibiting the combination $\infty P . [\infty P\infty] . \infty P\infty$. It melts at 106·5°, solidifies from fusion in the crystalline form, and volatilises with an acid, cough-exciting odour, but does not volatilise with vapour of water. It dissolves in 692·5 pts. of water at 19·1°, and its neutral salts do not produce any precipitate in solutions of manganous salts, whereas cinnamic acid melts at 133·4°, dissolves in 3,500 pts. water at 17°, and immediately precipitates manganous salts. Atropic acid heated with *potassium bichromate* and *sulphuric acid* forms benzoic acid, and further resembles cinnamic acid in its behaviour to *bromine*, of which it takes up 2 atoms.

The solution of atropic acid in aqueous *ammonia* leaves on evaporation an acid residue only partially soluble in water. The *potassium salt* forms shining laminæ soluble in alcohol. The *silver salt* $C^9H^7AgO^2$ crystallises from hot water in nodules. The *calcium salt* $C^{18}H^{14}CaO^4.5H^2O$ separates by slow evaporation in large monoclinic prisms, having a bright vitreous lustre, and exhibiting the combination $oP . [P\infty] . +nP\infty . \infty P\infty$, and with the approximately determined angles $oP : [P\infty] = 160°$; $oP : +nP\infty = 129°$; $oP : \infty P\infty = 77°–78°$. The crystals are tabular from predominance of oP, and cleave parallel to this face. The salt effloresces slowly in the air, more quickly over oil of vitriol, but does not become perfectly anhydrous till heated to between 190° and 200°, and then quickly takes up about 12 p. c. water from the air. It dissolves in 42 to 44 pts. water at 18° (calcium cinnamate in 608 pts.). There appear also to be calcium-salts of atropic acid which contain smaller quantities of water and give it up more easily (Kraut). Lossen describes a salt, $C^{18}H^{14}CaO^4.2H^2O$, which crystallises imperfectly in needles.

Atropic acid is resolved by oxidation with potassium dichromate and sulphuric acid into benzoic acid and carbon dioxide, with a trace of formic acid. When 2 grms. of it are fused with 40 grms. potassium hydrate till a brisk evolution of gas takes place, a small quantity of a solid acid is produced resembling benzoic acid; but if the fusion be interrupted as soon as a bright-burning gas begins to escape, the products formed are formic and alphatoluic acids. Atropic acid, heated to 137° for six hours with hydrochloric acid of sp. gr. 1·18, forms an amorphous chlorinated acid, together with an acid which is precipitated from its alkaline solution by mineral acids, dissolves in ether and in benzol, and is converted by prolonged boiling with water into isatropic acid. Possibly an additive product of atropic acid with hydrochloric acid is formed in the first instance. Atropic acid is converted by sodium-amalgam into an acid, $C^9H^{10}O^2$, which is different from homotoluic acid, forms a very soluble calcium salt, and a silver salt, $C^9H^9AgO^2$, crystallising from boiling water in scales. From these facts Kraut infers that atropic acid has the constitution represented by the formula $C''H.CH(C^6H^5).COOH$, containing a bivalent carbon-atom (*Zeitschr. f. Chem.* [2] v. 147).

Isatropic Acid, $C^9H^8O^2$, is produced, as above mentioned, by the action of baryta-water on tropic acid; also by heating the latter for several hours to 140° with strong hydrochloric acid. It differs considerably in its properties both from atropic and from cinnamic acid. It is nearly insoluble in cold water, dissolves but slightly in boiling water and in ether, and is still less soluble in alcohol than atropic acid. It suffers no loss of weight at 120°, and does not melt till heated to about 200°, whereas atropic acid melts at about 106° and sublimes at a slightly higher temperature. When precipitated from its alcoholic solution by water, it gradually forms microscopic thin rhombic laminæ.

Base obtained from Atropine.—Commercial atropine does not dissolve completely in boiling baryta-water, but separates oily drops, which on cooling form a resinous mass, consisting of a base, $C^{18}H^{23}NO^4$, the chloroplatinate of which crystallises from boiling water in small yellow needles (Kraut, *Ann. Ch. Pharm.* cxlviii. 236).

ATROSIN. A black substance contained in small quantity, according to F. Hübschmann (*Chem. Centr.* 1863, p. 864), in the alcoholic extract of the root of deadly nightshade, from which it is precipitated by ammonia. It is insoluble in water, alcohol, and ethor, but dissolves in aqueous acids, and is precipitated therefrom as a black powder by ammonia. Hübschmann supposes that this substance in the pure state forms the deep black of the ripe deadly nightshade berries, and in combination with an acid, the red colour of the juice.

AUERBACHITE. This name is given by R. Hermann (*J. pr. Chem.* lxxiii. 209) to a zirconium silicate occurring in the silicious slate in the Circle of Mariupel, Government of Jekaterinoslaw. It forms small quadratic octohedrons, having the angle P : P in the lateral edges = 86½°–87°; in the terminal edges = 121°. Colour brownish grey. Sp. gr. = 4·06. Hardness = 6·5 (Hermann), 7·5 (Kokscharow, *Jahresb.* 1860, p. 756). It gave by analysis 42·91 p. c. SiO^2, 55·18 ZrO^2, 0·93 FeO, and 0·95 loss by ignition (= 99·97), whence it appears to consist of $2ZrO^2.3SiO^2$, and to contain one-half more silica than zircon. It likewise differs from zircon, with which it is isomorphous, by its greater hardness and density.

AUGITE. On the composition of augite and amphibole (hornblende), see G. Tchermak (*Deut. Chem. Gesells. Berlin.* 1869, p. 384; *Zeitschr. f. Chem.* [2] v. 633).

AURICHALCITE. A copper-zinc bloom allied to aurichalcite is described by Risse and Braun (*Jahresb.* 1862, p. 759). It occurs at Guipuzcoa in Spain, in crystallo-radial and fibrous light-blue aggregates imbedded in calamine. Its analysis gave 13·41 p. c. CuO, 55·29 ZnO, 14·08 CO^2, 10·30 H^2O, and 1·86 residue (= 100·44), leading to the formula $(Cu;Zn)''CO^3.2Zn''H^2O^2$.

AURINE. A commercial name of rosolic acid (q.v.).

AUROSACETYL OXIDE. See ACETYLENE (p. 36).

AUSTRACAMPHENE.
AUSTRALENE. } See TURPENTINE OIL (v. 921, 924, 925).
AUSTRAPYROLENE.

AUTUNITE. *Uranite, Lime-uranite, Uranium mica, Calcio-uranic Phosphate.*—From analyses by Laugier (*Ann. Ch. Phys.* [3] xxiv. 239) and Pisani (*Compt. rend.* lii. 817; *Jahresb.* 1862, p. 1030), this mineral appears to contain 21 p. c. water, instead of 15 p. c. as formerly supposed. According to Pisani, the amount of water is reduced to 15 p. c. when the mineral is dried at 70°, but remains unaltered when it is kept at ordinary temperatures, even for months. In the mineral from Autun, Pisani found:

P^2O^5	U^2O^3	CaO	H^2O	Sum
13·4	56·47	5·60	20·10	3·20 = 98·67
14·0	59·0	5·8	21·2	— = 100·0

These numbers lead to the formula $CaO . 2U^2O^3 . P^2O^5 . 12aq.$ or $Ca''(\overset{''}{U^2}O^2)^2P^2O^8 . 12aq.$ Accordingly, autunite is not analogous in composition to chalcolite or cuprico-uranic phosphate, which contains only 8 molecules of water (iv. 585). Moreover, Descloizeaux has shown that the two minerals are dissimilar in crystalline form, chalcolite being dimetric, whereas autunite is trimetric. In small crystals from Cornwall he found the form to be derivable from a rhombic prism of 90° 43′, and exhibiting the combination $oP . \breve{P}\infty . \bar{P}\infty . \frac{1}{2}P$, with the angles $oP : \breve{P}\infty = 109° 19'$; $oP : \frac{1}{2}P = 116° 14'$ (*Ann. Min.* [5] xiv. 339; *Jahresb.* 1858, p. 724).

AVORNIN. This name is given by Kubly (*Zeitschr. f. Chem.* 1867, p. 26) to a glucoside which he has obtained (though not pure) from the bark of *Rhamnus frangula*, as an amorphous, easily fusible, brown or black mass, giving by analysis numbers agreeing with the formula $C^{15}H^{18}O^8$, and separable by acids into sugar, crystallisable, aurora-red avornic acid, $C^{11}H^9O^4$, and an amorphous resin. According to Faust (*Zeitschr. f. Chem.* [2] v. 18), avornin and avornic acid are identical with frangulin and frangulic acid respectively.

AXIN. A fat obtained in Mexico by boiling a species of coccus. (See ADDITIONS, vol. v. p. 1087.)

AZADIRACHTA INDICA. The almonds of this plant yield 41·5 p. c. of a yellow oil having a bitter taste, an alliaceous odour, sp. gr. 0·921, and solidifying at + 7°. By saponification it yields 35 p. c. of fatty acids melting at 30°, and 65 p. c. melting at 44°.

AZALEÏN. One of the varieties of aniline red.

AZELAIC ACID. $C^9H^{14}O^4$.—This acid agrees in composition and most of its properties with anchoic or lepargylic acid, but differs from it in its melting point, which is 8° or 10° lower (iii. 572). According to Overbeck (*Ann. Ch. Pharm.* cxl. 39; *Jahresb.* 1866, p. 332), it is produced, together with azelaic aldehyde, $C^9H^{16}O^3$, and stearoxylic acid, $C^{18}H^{32}O^4$, by the action of fuming nitric acid on stearoleic acid (q.v.). The azelaic acid and aldehyde remain in the alcoholic mother-liquor left after the first crystallisation of the stearoxylic acid. This liquid after some time deposits an oil which has a peculiar ethereal odour, and after distillation with water is nearly colourless, mobile, and insoluble in water. It is not saponified by alkalis, and in alcoholic solution forms with ammoniacal silver nitrate a precipitate which turns black when heated. It is not altered by nitric acid, but in contact with bromine and water it is gradually converted into azelaic acid. It exhibits the composition of azelaic aldehyde.

AZELAIC ALDEHYDE. See the last article.

AZO-AMIDOCHRYSAMMIC ACID. See CHRYSAMMIC ACID.

AZO-AMIDODRACYLIC ACID. See DRACYLIC ACID, under BENZOIC ACID.

AZO-ANISIC ACID. See ANISIC ACID (p. 173).

AZOBENZENE. See BENZENE.

AZOBENZOIC ACID. See BENZOIC ACID.

AZO-COMPOUNDS. The constitution, general properties, and modes of formation of these compounds are described under AROMATIC SERIES (p. 208).

AZOCONHYDRINE. $C^{32}H^{64}N^8O^4$. See vol. ii. ADDENDA (p. 964).

AZOCYMENE. See CYMENE-DERIVATIVES, and BENZENE, HOMOLOGUES OF.

AZODINAPHTHYL-DIAMINE. See NAPHTHYLAMINES.

AZODIOXINDOL. See ISATIN.

AZODIPHENYL-DIAMINE. Syn. with DIAZOAMIDOBENZENE (iv. 459).

AZODRACYLIC ACID. See DRACYLIC ACID, under BENZOIC ACID.

AZOPHENYLAMINE. Syn. with DIAZOBENZENE (iv. 430).

AZOROSANILINE. $C^{20}H^{10}N^6 = C^{20}(H^{10}\overset{'''}{N}{}^3)N^3$ (Caro a. Wanklyn, *Chem. Soc. J.* [2] iv. 324).—A base related to rosaniline in the same manner as azophenylamine (diazobenzene) to aniline, and produced in like manner by the action of nitrous acid on a salt of rosaniline:

$$C^{20}H^{19}N^3 + 3NHO^2 = C^{20}H^{10}N^6 + 6H^2O.$$

It resembles azophenylamine in yielding explosive salts, and when boiled with hydrochloric acid, it is converted into rosolic acid, which is related to rosaniline in the same manner as phenol to aniline:

$$\underset{\text{Azorosaniline.}}{C^{20}H^{10}N^6} + 3H^2O = \underset{\text{Rosolic acid.}}{C^{20}H^{16}O^3} + N^6.$$

AZOTOLUENE. See Toluene-derivatives, under Benzene, Homologues of.

AZOXINDOL. See Isatin.

AZOXYBENZENE. See Benzene.

AZOXYBENZOIC ACID. See Benzoic Acid.

AZOXYLENE. See Xylene-derivatives, under Benzene, Homologues of.

AZOTOLUENE and **AZOXYTOLUENE.** See Toluene-derivatives, under Benzene, Homologues of.

AZULENE or **CÆRULEIN.** A deep blue substance contained in many essentials oils (iv. 185).

AZULIN or **AZURIN.** A blue colouring matter obtained by boiling *péonine stable* (iv. 324) with aniline.

AZYMIC. A term applied by Pasteur to those infusoria which act as ferments only in presence of air, those which act independently of the air being called *zymic*.

B

BALATA. A substance resembling caoutchouc and gutta-percha, obtained from the dried milky juice of the Bully-tree of Guiana (*Sapota Muelleri*) (Sperling, *Zeitschr. f. Chem.* [2] v. 480).

BALSAMS. See Copaiba and Peru Balsam.

BARANILINE. This name is applied by Reimann (*Dingl. pol. J.* clxxxv. 49; *Jahresb.* 1867, p. 960) to the aniline oil prepared from crude benzol boiling between 100° and 150°, that which is obtained from benzol boiling below 100° being called *cuphaniline*. According to Reimann, the best yield of aniline red is obtained from a mixture of 3 pts. cuphaniline and 1 pt. baraniline, or approximately, 3 pts. aniline to 1 pt. toluidine.

BARBITURIC ACID. See Uric Acid, Derivatives of (v. 962).

BARAMMONIUM. A compound of barium and ammonium, described under Sodammonium (v. 320).

BARIUM. Crookes (*Chem. News*, vi. 194) prepares metallic barium as follows: A saturated solution of the chloride is heated to 93° with sodium-amalgam; the supernatant liquid is decanted from the amalgam thereby produced; and this amalgam is again boiled with the barium solution, then freed from salts by kneading under water, and from excess of mercury by pressure in a cloth. The very compact crystalline amalgam thus produced is placed in a bent tube under petroleum, and this liquid, together with the mercury, is removed by distillation, the heat being ultimately raised to redness. The metallic barium which remains tarnishes quickly on exposure to the air, and is gradually oxidised to pulverulent baryta; when scratched under petroleum, it exhibits metallic lustre. In water it gradually sinks and oxidises, with violent disengagement of hydrogen. In an alcohol flame it burns with red-green colour.

Barium Alcoholate, $Ba(C^2H^5O)^2$, separates on boiling an alcoholic solution of baryta. It can only be dried in an atmosphere of perfectly dry hydrogen gas at 100°. In contact with the liquid in which it has been formed, it redissolves on cooling, yielding a solution more concentrated than the original. A solution thus formed contained 2·188 grms. barium oxide in 10 cub. cent., and had a sp. gr. of 1·031 (Berthelot, *Bull. Soc. Chim.* [2] viii. 289).

Barium Alloys. When an alloy of sodium with *lead*, *tin*, *bismuth*, or *antimony* (not containing more than a third of its weight of sodium) is introduced into a crucible in which barium chloride is fused at a strong red heat (the quantity of the barium chloride being more than equivalent to the sodium contained in the alloy), the heat continued for a few seconds longer, and the crucible then removed from the fire, a crystalline alloy of barium and the heavy metal is produced containing only a trace of sodium. An alloy thus prepared with sodium bismuthide and barium chloride contained 28 p. c. barium. Such alloys may also be prepared without the use of reduced sodium, by heating an intimate mixture of sodium carbonate, charcoal, barium chloride, and finely divided tin, &c., as long as vapours of sodium continue to escape. The same methods serve for the preparation of alloys of tin, antimony, &c., with strontium and calcium. The alloys of the earth-metals thus obtained are not decomposed by strong heating in a crucible lined with charcoal; they oxidise quickly in the air, and if they contain more than 5 p. c. of the earth-metal, decompose water with facility, the other metal then remaining unattacked, in the form of a black powder; those which contain antimony give off gaseous hydrogen antimonide (Caron, *Compt. rend.* xlviii. 440; *Jahresb.* 1859, p. 129).

A crystalline alloy of barium and *aluminium* is obtained by heating baryta with aluminium and a small quantity of barium chloride. This alloy, which contains 23 or 24 p. c. barium, is somewhat darker-coloured than aluminium, and exhibits a yellow reflex on some of its faces; it decomposes water quickly at ordinary temperatures, forming a solution which does not exhibit any alkaline reaction, probably because the baryta and alumina unite to form an aluminate (Beketoff, *Bull. Soc. Chim.* 11 mars 1859).

A *platinum* wire plunged into fused barium chloride, and attached to the negative pole of a battery, the current of which is passing through the chloride, becomes covered with a yellow brittle alloy of barium and platinum, which slowly decomposes water, leaving platinum in the form of a fine powder (Matthiessen, *Chem. Soc. J.* viii. 294).

Caron (*Compt. rend.* l. 547) obtained an alloy of barium and *zinc* by melting zinc with barium chloride and sodium.

Barium Bromide. The hydrated bromide $BaBr^2.2H^2O$ crystallises, according to Handl (*Jahresb.* 1859 p. 132), in rhombic combinations of a prism of 106° 8′ and 73° 52′, having the acute edges truncated, and terminated at both ends by several pyramids and brachydomes. Rammelsberg (*Pogg. Ann.* cxxii. 616; *Jahresb.* 1864, p. 189) refers the crystals to a primary form in which the axes $a : \breve{b} : c$ = 0·3758 : 1 : 0·4348 (Handl's prism of 106° 8′ and 73° 52′ then becoming $\infty\breve{P}2$). He observed combinations of P . $3\bar{P}3$. $\infty\breve{P}2$. $\bar{P}\infty$. $3\bar{P}\infty$. $\bar{P}\infty$. $\infty\breve{P}\infty$. Angle P : P (brach.) = 148° 16′; P : P (macr.) = 86° 36′; P : P (basal.) = 102° 2′. The hemimorphous and partial development of the crystals gives them a monoclinic character; and in fact G. Werther (*J. pr. Chem.* xci. 167) supposed them to belong to the monoclinic system.

The specific gravity of anhydrous barium bromide is 4·23; of the hydrated salt, 3·690 (H. Schiff, *Jahresb.* 1858, p. 11).

The specific gravities (referred to water at 19·5° as unity) of solutions of barium bromide of various strengths have been determined by Kremers (*Jahresb.* 1857, p. 67) with the following results:

$BaBr^2$ in 100 pts. water .	17·81	38·83	60·92	81·97	104·68
Sp. gr. of solution .	1·1440	1·3005	1·4507	1·5816	1·7115

Barium Chloride. Sp. gr. of the anhydrous chloride $BaCl^2$ = 3·82; of the hydrated chloride, $BaCl^2.2H^2O$ = 3·052 (Schiff, *loc. cit.*); 3·081 (Buignet, *Jahresb.* 1861, p. 15).

Specific Gravities of Aqueous Solutions of Barium Chloride.

Kremers *		Gerlach †		Schiff ‡	
Percentage of $BaCl^2$	Sp. gr. (water at 19·5° = 1)	Percentage of $BaCl^2$	Specific gravity at 15°	Percentage of $BaCl^2.2H^2O$	Specific gravity at 21·5°
8·88	1·0760	5	1·0458	3·50	1·0261
18·24	1·1521	10	1·0951	7·00	1·0531
27·53	1·2245	15	1·1485	10·51	1·0816
35·44	1·2837	20	1·2061	14·01	1·1123
		25	1·2702	21·02	1·1770
		25·97	1·2827	31·53	1·2878

Respecting the solubility of barium chloride in aqueous alcohol of various strengths, see ETHYL ALCOHOL.

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* *Pogg. Ann.* xcix. 63; *Jahresb.* 1857, p. 67.

† *Spec. Gewichte der gebräuchlichsten Salzlosungen bei verschiedenen Concentrationsgraden.* Freiberg, 1859. *Jahresb.* 1859, p. 43.

‡ *Ann. Ch. Pharm.* cvii. 293; *Jahresb.* 1858, p. 38.

Barium Iodide. BaI^2.—Liebig prepares this salt by drenching 1 pt. of finely divided amorphous phosphorus in a porcelain dish with 40 pts. of warm water, gradually adding 20 pts. of dry iodine, and bringing it into contract with the phosphorus by trituration with a pestle. As soon as the originally dark brown liquid has become colourless (a change which may be accelerated by warming in the water-bath) it is to be decanted from the slight residue of phosphorus, and saturated with barium carbonate; baryta-water then added sufficient to produce a slight alkaline reaction; the liquid filtered from the separated barium phosphate; and the solution of barium iodide evaporated, any slight excess of baryta that it may contain being separated by absorption of carbonic acid during the evaporation (*Ann. Ch. Pharm.* cxxi. 222). G. Werther (*J. pr. Chem.* xci. 331) obtained this compound as a bye-product in the preparation of barium tetrathionate (v. 641), in rather large, well-defined crystals containing $BaI^2.2H^2O$, and isomorphous with the bromide; they are very deliquescent, and quickly turn red-brown in contact with the air. Werther did not obtain the heptahydrated crystals described by Croft (i. 504).

According to Kremers (*Jahresb.* 1858, p. 40), 1 pt. of anhydrous barium iodide dissolves in the following quantities of water at the temperatures under-mentioned:

Temperature	0°	19·5°	30°	40°	60°	90°	106°
Quantity of water	0·59	0·48	0·44	0·43	0·41	0·37	0·35

Solutions of various strengths were found by Kremers to have the specific gravities stated in the following table, referred to that of water at 19·5° as unity;

Quantity of BaI^2 in 100 pts. of water	Specific gravity of solution
27·0	1·2157
53·8	1·4099
85·8	1·6186
115·6	1·7953
146·0	1·9585

Respecting the expansions of solutions of barium iodide of various strengths, see Kremers, *Pogg. Ann.* cxi. 60; *Jahresb.* 1860, p. 47.

Barium Oxides. The *monoxide* or *Anhydrous Baryta*, BaO, may be prepared on the large scale by igniting a mixture of barium carbonate and charcoal in a reverberatory furnace, and directing a stream of oxygen gas on the hearth towards the end of the reaction; the remaining charcoal is thereby burnt, but in consequence of the high temperature the carbon dioxide produced is not absorbed by the baryta (atmospheric air cannot be substituted for pure oxygen in the process). The baryta thus obtained is said to be pure, with the exception of a small amount of alkali (Tessié du Mothay, *Bull. Soc. Chim.* [2] viii. 454). Rivière ignites barium sulphate with ⅛ of its weight of pounded coal; decomposes the barium sulphide by means of the carbonic acid gas produced in the reduction; and finally converts the precipitated barium carbonate into oxide by ignition with $\frac{1}{10}$ of its weight of coal; but, according to Scheurer-Kestner, the process does not yield very good results (*Bull. Soc. industr. de Mulhouse*, xxxvi. 446; *Jahresb.* 1867, p. 908).

Dioxide or *Peroxide.* BaO^2.—The dioxide prepared by passing oxygen over heated baryta, or by igniting baryta with potassium chlorate (i. 506), always contains a certain proportion of the monoxide. To obtain it pure, Brodie (*Proc. Roy. Soc.* xii. 655) converts the crude peroxide produced by either of the methods just mentioned into a hydrate by trituration with water; then gradually supersaturates it with dilute hydrochloric acid; mixes the filtered solution, first with a slight excess of baryta-water, and then (after quickly filtering off the precipitate of alumina and ferric oxide through linen) with more baryta-water, whereby the hydrated dioxide is thrown down in shining laminæ. It is insoluble in water, and when pressed between paper and dried under the air-pump, gives off its water and leaves the anhydrous dioxide, in the form of a white perfectly stable powder resembling magnesia.

Barium dioxide is decomposed by the sulphates of the alkali-metals, yielding barium sulphate and a hydrate of the alkali-metal, together with rapidly diminishing quantities of hydrogen dioxide; with alkaline carbonates in slight excess, the hydrogen dioxide produced is somewhat more stable (Weltzien, *Jahresb.* 1866, p. 110). With ethylsulphuric acid, it yields ethyl oxide and ethylene gas (Baudrimont, *Compt. rend.* lxii. 829).

The chlorides and oxides of oxygenated organic radicles are converted by barium dioxide into the corresponding peroxides (Brodie). See vol. iv. p. 309.

BATHVILLITE. A substance of organic origin, occurring in the coal-measures of the neighbourhood of Bathville (bordering on the Torbane Hill district) in brown brittle lumps of sp. gr. 1·010. It is infusible and does not yield anything to benzol. Moderately dilute nitric acid has no action upon it, but strong sulphuric acid, with aid of heat, chars it completely. Heated in a platinum crucible, it emits a fatty odour, gives off gases which burn with a smoky flame, and leaves a pure white ash. Its analysis gave

C	H	N, O, S, &c.	Ash	
58·89	8·56	7·23	25·32	= 100

or, calculated on the substance free from ash, C 78·86, H 11·46. The difference from 100 being reckoned as oxygen, the composition answers to the formula $C^{30}H^{50}O^{3}$ (C. Gr. Williams, *Chem. News*, vii. 153).

BAUXITE. This name was originally applied by Berthier (*Ann. Min.* [5] vi. 531) to a ferruginous aluminic hydrate, containing 55·4 p. c. alumina and 44·5 ferric oxide, occurring in roundish masses in the crystalline limestone of Baux, near Arles, in France. This mineral fused with alkalis gives traces of vanadic acid (H. Deville, *Ann. Ch. Phys.* [3] lxi. 309).

Analyses of bauxite and allied minerals have been made by M. v. Lill (*Jahresb.* 1866, p. 923), Schnitzer (*Dingl. pol. J.* clxxxiv. 329; *Jahresb.* xx. 982), and H. Deville (*Ann. Ch. Phys.* [3] lxi. 321, 324).

BAYLDONITE. A hydrated arsenate of lead and copper from Cornwall, occurring in small warty concretions, of grass-green or blackish-green colour, slightly conchoïdal fracture, and more or less distinct resinous lustre. Hardness = 4·5. Sp. gr. = 5·35. Analysis gave 30·13 p. c. PbO, 30·88 CuO, 31·76 As^2O^5, 4·58 H^2O, with 2·65 ferric oxide and loss, leading to the formula $PbO.3CuO.As^2O^5.2H^2O$ or $PbCu^2(AsO^4)^2.CuH^2O^2.H^2O$ (Church, *Chem. Soc. J.* [2] iii. 265).

BEAN. The bean from which Dr. Stenhouse obtained bases (apparently of the pyridine series) by destructive distillation (*Phil. Mag.* [3] xxxv. 534) was the kidney-bean (*Phaseolus vulgaris*), not the common field-bean (*Faba vulgaris*) as originally stated (*Communication from Dr. Stenhouse*).

BEAUMONTITE. Descloizeaux (*Ann. Min.* [5] xi. 261) concludes from the optical properties of this mineral that it is identical with heulandite (stilbite). See STILBITE (v. 433).

BEBIRINE or **BEBEERINE.** According to J. Trupp (*Jahresb.* 1863, p. 702), this alkaloïd gives with phosphomolybdic acid a yellow precipitate, which dissolves in ammonia, forming a blue solution which becomes colourless on boiling.

According to Walz (*N. Jahrb. Pharm.* xiv. 15; *Jahresb.* 1860, p. 548), buxine, the alkaloïd obtained from the leaves and other parts of *Buxus sempervirens*, is identical with bebirine, the analysis of the alkaloïd itself, and of its hydrochloride, platinochloride, and mercurochloride, leading to the formula of bebirine $C^{19}H^{21}NO^3$. The alkaloïd dissolves in 6,000 pts. of cold water, forming a feeble alkaline solution, in 1,800 pts. of boiling water, in 2 to 3 pts. alcohol of sp. 0·85, in 5·2 pts. of anhydrous alcohol, and in 13 pts. of pure ether, the alcoholic and ethereal solutions being strongly alkaline. It remains in the amorphous state when its solutions are evaporated, and all its salts are uncrystallisable.

According to Flückiger (*Zeitschr. f. Chem.* [2] vi. 251), parisine obtained by Winckler from a cinchona-bark, and pelosine from the root- and stem-bark of *Cissampelos Pereira* and *Botryopsis platyphylla* are likewise identical with bebirine. This alkaloïd is especially distinguished by the readiness with which it is precipitated from solution in hydrochloric acid by potassium nitrate, ammonium chloride, and potassium iodide.

BECKITE. For Church's observations on this mineral, see *Phil. Mag.* [4] xxiii. 95.

BECUIBIC ACID. A crystallisable acid contained, together with gum, resin, and tannin, in the red juice of *Myristica bicuhyba* (Th. Peckolt, *Chem. Centr.* 1861, p. 726).

BEER. A large number of analyses, recently made, show that in the various classes of malt-liquor sold in London there is a variation in the amount of alcoholic contents from 3·87 to 8·41 per cent. of absolute alcohol by weight, these two extremes corresponding to ·98 and 2·18 fluid ounces of absolute alcohol in the pint of beer. The amount of extract varies from 2·16 to 13·32 per cent. by weight, or from ·73 to 2·77 ounces per pint of beer, as will be seen from the accompanying table.

Kind of malt liquor	Specific gravity	Percentage of			Original gravity of wort	Malt per barrel	Contents per pint		
		Alcohol	Extract	Acetic acid			Alcohol fl. oz.	Extract ozs.	Acid grs.
Burton ale (Allsopp's) .	1040·38	8·25	13·32	·32	1121·63	4·50	2·16	2·77	29·12
Bass's barley wine.	1032·31	8·41	11·75	·23	1114·78	4·25	2·18	2·42	20·77
Edinburgh ale.	1006·63	4·41	3·58	·19	1048·38	1·77	1·12	·72	16·73
Guinness's stout	1015·51	6·81	6·17	·24	1078·06	2·88	1·74	1·25	21·32
Truman, Hanbury, & Co.'s porter	1013·16	4·02	5·12	·24	1051·33	1·90	1·03	1·01	21·27
Whitbread's porter	1014·04	4·28	5·15	·18	1054·11	2·00	1·09	1·03	15·97
Hoare's porter .	1012·99	4·18	5·04	·18	1052·42	1·94	1·06	1·03	15·95
Perry's ale. . .	1006·48	3·87	3·65	·14	1045·82	1·69	0·98	0·73	7·97

The relative proportions of alcohol and extract also differ according to the class of malt-liquor, and independently of the actual strength measured by the quantity of malt per barrel used in brewing. Thus, for instance, pale ale, as a rule, contains less extract relatively to the alcohol than old or mild ale. This difference is chiefly due to the way in which the fermentation is conducted, and to its being carried further in the brewing of pale ale than it is in other cases.

In comparing the results of analysis, with the object of judging as to the quality of beer, some considerable allowance must be made for those differences in the character of beer which are not clearly expressed by the amount either of alcohol or of extract, nor even by the proportion of malt used in brewing, as indicated by the estimated original gravity. In this respect, the system of brewing adopted in particular cases may be of far greater influence in determining the quality and character of beer than the mere amounts of alcohol and of extract that it contains; but, subject to this influence, the amount of malt indicated by the estimated original gravity of beer, as having been used in the brewing, may be regarded as the best approximative test of quality. It must, however, be borne in mind that sugar is now largely used in brewing as a substitute for malt, and that there are no means of ascertaining by analysis when this is the case.

The relative proportions of alcohol and extract in beer will also have some influence on its fitness in a medical point of view for certain persons; and in some instances thin dry beer that has had the fermentation carried so far as to reduce the amount of extract to a minimum, may be very preferable to beer containing a larger amount of extract. In this respect, some samples of the Prestonpans beer are remarkable for the small proportion of extract they contain.

In regard to the nutritive value of beer, over and above the stimulant and tonic actions due to the alcohol and to the bitter principle of the hop, it is worth notice that a pint of pale ale contains from $\frac{1}{2}$ an ounce to 1 ounce of solid extract, while mild and old ale contain from $1\frac{1}{10}$ to $2\frac{3}{4}$ ounces in the pint.

The amount of free acid in British beer appears to be uniformly larger than in the Viennese and Bavarian beer recently introduced here, and sometimes it is very much larger. This free acid is represented in the tables as acetic acid; but there is reason to believe that beer probably contains lactic acid or other fixed acids, together with a substance analogous to glucic acid, which, according to Graham, Hofmann, and Redwood, appears to be produced in the fermentation of beer-wort, as practised in this country.

There appear to be great differences in the quality of beer sold by publicans at a given price. Thus, for instance, the variation in the pale ale sold at fourpence per pint is from 4·08 to 7·10 per cent. of alcohol, and from 3·22 to 7·53 per cent. of extract; in the mild ale sold at twopence per pint it is from 4·43 to 5·62 per cent. alcohol, and from 5·01 to 5·56 per cent. of extract; and in old ale sold at fourpence per pint it is from 6·20 to 8·31 per cent. of alcohol, and from 4·56 to 6·2 per cent. of extract. These differences represent respectively 1·58, ·27 and ·49 bushels of malt per barrel of the beer.

From the great alcoholic strength of some kinds of old ale, they partake more of the nature of wine than of beer, in the usual sense of this term. They are, in fact, quite equal in that respect to most of the cheaper wine imported from the Continent, while, in flavour and general character, old ale, such as that brewed at Burton-on-Trent and in Scotland, is far superior to any wine of the kind referred to, which can be sold here at a price even double that of the best old ale. This kind of ale, however, is but rarely sold by publicans. B. H. P.

BENOLIC ACID. $C^{22}H^{40}O^2$ (Hausknecht, *Ann. Ch. Pharm.* cxliii. 40).—An acid produced by the abstraction of the elements of hydrogen bromide from bromide of erucic acid, $C^{22}H^{42}O^2Br^2$. When this latter compound is enclosed in a sealed tube together with 4 or 5 mol. of potassium hydrate in alcoholic solution, and heated to 145° for seven or eight hours, the product, after cooling, dissolved in water, and hydrochloric acid added, benolic acid separates, and may be obtained by recrystallisation from alcohol in tufts of white needles. It melts at 57·5°, becomes electric when rubbed, dissolves easily in ether and in absolute alcohol, less easily in cold aqueous alcohol, and is insoluble in water. It does not take up hydrogen when heated with sodium-amalgam.

The benolates of the alkali-metals are soluble in water, the rest insoluble. The *potassium* and *sodium salts* form nodular crystals; the *ammonium salt* separates from dilute alcoholic solution in colourless laminæ, which soon give off ammonia and become opaque. The *silver salt* $C^{22}H^{39}AgO^2$ is insoluble in water and in alcohol. The *barium salt* $Ba(C^{22}H^{39}O^2)^2$, obtained by precipitating barium chloride with the acid, is insoluble in water, alcohol, and ether. The *strontium* and *calcium salts* resemble it. The *magnesium salt* is precipitated by the acid from an alcoholic solution of magnesium acetate, and separates from boiling alcohol in crystals containing $Mg(C^{22}H^{39}O^2)^2.3H^2O$. It is efflorescent, and melts at 130° with loss of its crystallisation-water.

As erucic acid, which belongs to the acrylic series, is bivalent, benolic acid, which is derived from it by abstraction of H^2, must be quadrivalent. Accordingly it forms a dibromide and a tetrabromide.

The dibromide, $C^{22}H^{40}Br^2O^2$, is produced, with slight evolution of hydrobromic acid, when rather more than 1 mol. of bromine is gradually added to 1 mol. of the benolic acid. It forms shining white laminæ, melting between 46° and 47°, heavier than water, easily soluble in alcohol and ether. Heated for several hours with alcoholic potash in a sealed tube to 150° (not in the cold), it gives up bromine and appears to be chiefly reconverted into benolic acid; an acid containing less hydrogen does not appear to be formed.

The tetrabromide, $C^{22}H^{40}Br^4O^2$, is formed, with violent hissing and copious evolution of hydrobromic acid, when benolic acid is added by small portions to excess of bromine, and separates as a fused, afterwards solidifying mass, which may be purified by solution in soda-ley, precipitation with hydrochloric acid, and crystallisation from alcohol. It forms white shining laminæ, melting at 77° to 78°. It is decomposed by alcoholic potash, but without yielding any definite products. Sodium-amalgam at the boiling heat slowly withdraws the whole of the bromine, forming an acid melting at 33°, probably erucic acid.

Dioxybenolic Acid, $C^{22}H^{40}O^4$, is produced, together with another solid acid (brassylic acid) and a liquid oil (brassylic aldehyde), when red fuming nitric acid is added by drops to melting benolic acid; and if the semisolid product of the oxidation be carefully washed with water and then dissolved in hot absolute alcohol, the dioxybenolic acid crystallises out for the most part on cooling, while the other solid acid and the oil remain in solution, and separate out after some time only. Dioxybenolic acid is obtained by repeated crystallisation in small yellowish scales; it melts at 90°–91°, and solidifies again in the crystalline state. It is insoluble in water, less soluble in alcohol than benolic acid, not further attacked by nitric acid. It is monobasic. The dioxybenolates of the alkali-metals separate from alcoholic solution in crystalline crusts; those of the alkaline earth-metals are insoluble in water and in alcohol. The *silver salt* $C^{22}H^{39}AgO^4$ is a white precipitate not much affected by light.

BENZAMIDE. According to Petersen (*Ann. Ch. Pharm.* cv. 277), benzamide is formed on distilling a mixture of sodium benzoate and sal-ammoniac; according to J. Head, on the contrary (*Jahresb.* 1858, p. 314), no benzamide is formed under these circumstances, but a sublimate of benzoic acid is obtained, with evolution of ammonia; probably thus:

$$C^7H^5NaO^2 + NH^4Cl = C^7H^6O^2 + NH^3 + NaCl.$$

The crystals of benzamide obtained by melting it, and decanting the still fluid from the partially solidified portion, are tabular rhombic combinations, $\infty\bar{P}\infty$. ∞P . $\infty\bar{P}2$. $\infty\breve{P}\infty$. $P\infty$, having the axes *a* : *b* : *c* in the ratio 0·9338 : 1 : 0·227, and the angle $\infty P : \infty P$ (macr.) = 89° 4′; $\bar{P}\infty : \bar{P}\infty$ in the same = 153° 56′. Cleavage perfect parallel to $\infty \bar{P}\infty$ (G. vom Rath, *Pogg. Ann.* cx. 107).

Sulphuric anhydride converts benzamide into a brownish-yellow mass smelling of benzonitrile, and containing (together with unaltered benzamide) ammonia and sulphobenzoic acid, the benzamide being probably first resolved into ammonia, benzonitrile, and benzoic acid, which latter is then converted into sulphobenzoic acid. *Sulphuric chlorhydrate*, SO^3HCl, heated with benzamide, yields benzoic chloride, benzonitrile, benzoic acid, and probably also sulphobenzoic acid (Engelhardt, *Jahresb.* 1864, p. 350).

Benzamide boiled with *bromine* and water is converted into sal-ammoniac and bromobenzoic acid:

$$C^7H^7NO + H^2O + Br^2 = NH^4Br + C^7H^5BrO^2.$$

The bromobenzoic acid thus produced appeared to be a mixture of two isomeric acids, inasmuch as on recrystallisation the melting point rose from 149° to nearly 200° (W. Brauns, *Arch. Pharm.* [2] cxxvi. 214).

Benzamide gently heated with *phosphoric sulphide*, P^2S^5, yields a distillate of benzonitrile, and a residue probably consisting of cyaphenine mixed with phosphoric anhydride (L. Henry, *Zeitschr. f. Chem.* [2] v. 446).

Metachlorobenzamide, C^7H^6ClNO, is formed by triturating metachlorobenzoyl chloride (salyl chloride) with ammonium carbonate (Gerhardt a. Drion; see i. 540); also by the action of ammonia on ethyl metachlorobenzoate. It crystallises in very beautiful nacreous needles, soluble in alcohol and ether, very slightly soluble in boiling water, melting at 139°, and sublimable without decomposition (Kekulé, *Ann. Ch. Pharm.* cxvii. 145).

NITROBENZAMIDE, $C^7H^6(NO^2)NO$, is most easily obtained from the product of the action of phosphorus pentachloride on nitrobenzoic acid (after removal of the oxychloride at about 130°) by dropping this product into strong aqueous ammonia. It melts at 140° to 142°, and is converted, by treatment with ammonium sulphide, into amidobenzamide, $C^7H^6(NH^2)NO$ or oxybenzodiamide, $N^2(C^7H^4O)''H^4$, isomeric with phenyl-carbamide. This compound separates from solution in crystals containing $C^7H^8N^2O.H^2O$, which melt and give off their water at 75° (Beilstein, *Ann. Ch. Pharm.* cxxxii. 137). Compare Chancel's statements, under OXYBENZODIAMIDE (iv. 294).

Paranitrobenzamide (nitrodracylamide), prepared similarly to (ortho-) nitrobenzamide, is less soluble in water, and melts at 197° to 198°. By ammonium sulphide it is converted into para-amidobenzamide (amidodracylamide), which forms large light yellow crystals, $2C^7H^8N^2O.H^2O$, much less soluble in water than (ortho-) amidobenzamide, and melting at 178° to 179° with loss of 3·2 p. c. water. By boiling with potash, it is resolved into ammonia and para-amidobenzoic (amidodracylic) acid (Beilstein, *loc. cit.*).

THIOBENZAMIDE, C^7H^7NS, is converted by iodine into the compound $C^{14}H^{10}N^2S$, which crystallises from boiling alcohol in long colourless needles; melts at 90°; sublimes without decomposition at a higher temperature; is decomposed by boiling with alcoholic soda, the sulphur being separated as sodium hyposulphite; not altered by boiling with hydrochloric, nitric, or dilute sulphuric acid; but converted by boiling with moderately strong sulphuric acid into a base, $C^{14}H^{14}N^2$, which melts at 71° and forms crystallisable salts. Chlorine, bromine, and dilute nitric acid act upon thiobenzamide in the first instance in the same manner as iodine, but their action has a tendency to go further, giving rise to substitution-products (Hofmann, *Deut. Chem. Ges. Berlin.* 1869, 645; *Zeitschr. f. Chem.* [2] vi. 208).

DIAZOBENZAMIDE, $C^7H^5N^3O = N\left\{\begin{matrix}C^7H^3N^2O\\H^2\end{matrix}\right.$.—The nitrate of this amide, $C^7H^5N^3O.NHO^3$, is described in vol. iv. p. 295.

The nitrates of the isomeric compounds diazodracylamide and diazosalylamide are produced in like manner by the action of nitrous acid on amidodracylamide and amidosalylamide in ethereal solution.

DIAZOBENZIMIDE, $C^7H^5N^3O^2 = N\left\{\begin{matrix}(C^7H^4N^2O^2)''\\H\end{matrix}\right.$, is produced by the action of aqueous ammonia on the perbromide of diazobenzoic acid:

$$C^7H^4N^2O^2.HBr.Br^2 + 4NH^3 = 3NH^4Br + C^7H^5N^3O^2.$$

It crystallises in almost white thin laminæ, which dissolve easily in alcohol and ether, less easily in boiling water, scarcely at all in cold water, melting at 160°, and decomposing with slight detonation. It forms well-defined salts; the silver salt is a white amorphous precipitate.

Isomeric compounds are formed by the action of ammonia on the perbromides of diazodracylic and diazosalylic acid. *Diazodracylimide* likewise crystallises in laminæ, but melts at 185°. *Diazosalylimide* is moderately soluble in boiling water, and crystallises therefrom in long needles which melt at 145° and sublime at 100° (Griess, *Zeitschr. f. Chem.* [2] iii. 164).

DIBENZAMIDE or DIBENZOYLAMIDE, $C^{14}H^{11}NO^2 = N(C^7H^5O)^2H$, is produced, together with benzamide, by the action of potassamide on benzoyl chloride dissolved in anhydrous ether (iv. 695):

$$3C^7H^5OCl + 3NKH^2 = C^7H^7NO + C^{14}H^{11}NO^2 + 3KCl + NH^3.$$

The mass of colourless crystals thereby produced is freed from ether by distillation, and rapidly washed with cold water to remove potassium chloride: the residue, on recrystallisation from boiling water, separates into more soluble benzamide and less soluble dibenzamide. Dibenzamide crystallises in rhombic combinations of a pyramid with a secondary prism, soluble in 800 pts. of water at 15°, and melting at 138°. Its reactions are similar to those of benzamide (Beilstein a. Landolt, *Ann. Ch. Pharm.* cxi. 1). According to G. vom Rath (*Pogg. Ann.* cx. 107), the crystals exhibit the combination $P \,.\, \infty\breve{P}2$, with the axes $a : b : c$ in the ratio 0·9305 : 1 : 1·0690; and angle P : P (brach.) = 109° 50′; P : P (macr.) = 103° 45′; $\infty\breve{P}2 : \infty\breve{P}2$ (macr.) = 123° 30′. Cleavage perfect parallel to $\infty\breve{P}\infty$.

BENZANILIDE and **DIBENZANILIDE.** See PHENYL-BENZAMIDES (iv. 476).

BENZANILIDYL CHLORIDE. This name was given by Gerhardt (*Ann. Ch. Phys.* [3] liii. 307) to a compound obtained by the action of phosphorus pentachloride, assisted by a gentle heat, on benzanilide (iv. 476). A brisk reaction takes place; hydrochloric acid is evolved; phosphoric oxychloride distils over; and the small quantity of that compound remaining in the liquid product may be removed by adding a small piece of phosphorus, whereby it is converted into phosphorous chloride, PCl^3, which is easily driven off by a gentle heat. Benzanilidyl chloride, $N(C^7H^5)'''(C^6H^5)Cl$, then remains in the form of a viscid mass, which colours flame green, fumes in the air, is decomposed by water and aqueous alcohol, with formation of benzanilide, dissolves without decomposition in ether, and is resolved by heat into benzonitrile, NC^7H^5, and phenyl chloride, C^6H^5Cl. Heated with excess of *aniline*, it gives off hydrochloric acid and forms a solid mass, consisting of a diamide, $C^{19}H^{16}N^2$ or $N^2(C^7H^5)'''(C^6H^5)^2H$. If, on the other hand, the chloride is in excess, the resulting thick mass, treated with boiling alcoholic potash, gives off the odour of phenol and forms an alkaline solution containing salicylic acid:

$$\underset{\text{Diamide.}}{C^{19}H^{16}N^2} + KHO + 4H^2O = \underset{\text{Phenol.}}{2C^6H^6O} + \underset{\substack{\text{Potassium}\\ \text{salicylate.}}}{C^7H^5KO^3} + 2NH^3 + H^2.$$

Benzanilidyl chloride is violently attacked by dry ammonium carbonate, and the solid product, after being washed with water, yields to boiling alcohol a solution from which benzanilidylamide crystallises in brownish-yellow radiate nodules, which are but slowly attacked by alcoholic potash solution, even at the boiling heat.

BENZENE or **BENZOL.**[*] C^6H^6. *Formation.*—1. From other hydrocarbons. α. Acetylene, heated in a bent glass tube over mercury to the softening point of the glass, is converted into a number of polymeric hydrocarbons, among which is benzene, forming about half the entire liquid product: $3C^2H^2 = C^6H^6$. Benzene may therefore be regarded as triacetylene (Berthelot). See ACETYLENE (p. 32).—β. Toluene, C^7H^8, passed through a red-hot porcelain tube yields a liquid distillate containing a considerable quantity of benzene, together with naphthalene:

$$4C^7H^8 = 3C^6H^6 + C^{10}H^8 + 3H^2,$$

γ. Xylene, C^8H^{10}, and Cumene, C^9H^{12} (from coal-tar), similarly treated, yield benzene, together with some of its homologues and other hydrocarbons.—δ. Cinnamene or styrol, C^8H^8, passed through a red-hot tube is partly resolved into benzene and acetylene, $(C^6H^6 + C^2H^2)$. The same hydrocarbon heated in a sealed tube filled with hydrogen is resolved into benzene and ethylene:

$$C^8H^8 + H^2 = C^6H^6 + C^2H^4.$$

ε. Diphenyl, $C^{12}H^{10}$, heated in a tube filled with hydrogen is partly converted into benzene and chrysene, $C^{18}H^{12}$, the latter probably resulting from polymerisation of previously formed phenylene, C^6H^4:

$$C^{12}H^{10} = C^6H^6 + C^6H^4.$$

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[*] The term *benzene* will be used to denote the pure hydrocarbon C^6H^6; and *benzol* for the commercial product, containing also the higher homologues of benzene.

ζ. A mixture of diphenyl-vapour and ethylene passed through a red-hot tube is partly resolved into benzene and cinnamene:

$$C^{12}H^{10} + C^2H^4 = C^6H^6 + C^8H^8.$$

η. A mixture of chrysene-vapour and ethylene yields, under the same circumstances, benzene and anthracene, with a small quantity of naphthalene:

$$C^{18}H^{12} + C^2H^4 = C^6H^6 + C^{14}H^{10} \text{ (anthracene).}$$

$$C^{18}H^{12} + 2C^2H^4 = 2C^6H^6 + C^{10}H^8 \text{ (naphthalene).}$$

θ. Ethylene and anthracene also yield benzene and naphthalene:

$$C^{14}H^{10} + C^2H^4 = C^6H^6 + C^{10}H^8.$$

ι. Chrysene heated with hydrogen yields benzene and diphenyl:

$$C^{18}H^{12} + 2H^2 = C^6H^6 + C^{12}H^{10}.$$

2. From Menhaden oil (obtained from *Alosa Menhaden*, a kind of herring), which is resolved by the dry distillation of its lime-soap into benzene and its homologues, together with a number of hydrocarbons of the marsh-gas series (Warren and Storer, *Zeitschr. f. Chem.* [2] iv. 229).

3. From chlorobenzol, $C^7H^6Cl^2$, and from benzoic trichloride, $C^7H^5Cl^3 = C^6H^5(CCl^3)$, by heating with soda-lime (Limpricht, *Ann. Ch. Pharm.* cxxxix. 303; *Jahresb.* 1866, 593, 595):

$$C^7H^6Cl^2 + H^2O = C^6H^6 + CO + 2HCl$$

and

$$C^7H^5Cl^3 + 2H^2O = C^6H^6 + CO^2 + 3HCl.$$

4. From diazobenzene, by heating its nitrate or sulphate with alcohol, or the latter with alcoholic potash, aldehyde and other products being formed at the same time (Griess; *vide* iv. 432):

$$C^6H^4N^2 + C^2H^6O = C^6H^6 + C^2H^4O.$$

5. From bromobenzoic acid by distillation with lime (A. Riche, *Jahresb.* 1861, p. 615).

6. From cinnamic acid by distillation with a large excess of lime or baryta (D. Howard, *Chem. Soc. J.* xiii. 135).—7. From trimesic acid, $C^9H^6O^6$, by heating strongly with excess of lime: $C^9H^6O^6 = C^6H^6 + 3CO^2$ (Fittig a. Furtenbach, *Zeitschr. f. Chem.* [2] iv. 4).

Purification of Commercial Benzol.—When 1 vol. rectified coal-tar naptha, containing about 50 p. c. benzene, is mixed with 6 vol. strong sulphuric acid previously diluted with 1 vol. water, and the mixture is heated in a still, the hydrocarbons of higher boiling point dissolve for the most part in the acid, while the benzene remains unattacked. If lumps of pumice-stone are moistened with the acid, its action becomes more decided (Church, *Phil. Mag.* [4] xxi. 176).

E. Kopp (*Moniteur scientifique*, vi. 329) recommends for the purification of benzol, for conversion into nitrobenzol, aniline, &c., to cool it in Carré's refrigerator to −15°, press the resulting crystalline mass quickly, fuse it, and again subject it to the same treatment.

Berthelot (*Bull. Soc. Chim.* [2] vi. 289) enumerates the following properties of benzene as readily available for its separation from mixtures of hydrocarbons of which it forms only a small fraction: α. Its unalterability when heated in sealed tubes to 200°-400° (cinnamene, terebenthene, &c., pass under these circumstances into polymeric modifications of high boiling point).—β. Indifference towards iodine, saturated solutions of hydriodic and hydrochloric acids, and concentrated sulphuric acid, and its comparative indifference towards bromine.

Density.—Louguinine (*Ann. Ch. Phys.* [4] xi. 465) has given the following table of the densities and volumes of benzene at various temperatures:

Temperatures	Densities	Volumes
0°	0·8995	1·0000
5	0·8939	1·0063
10	0·8887	1·0122
15	0·8833	1·0183
20	0·8780	1·0245
25	0·8726	1·0308
30	0·8673	1·0371
35	0·8620	1·0435
40	0·8567	1·0500
45°	0·8512	1·0567
50	0·8468	1·0622
55	0·8402	1·0706
60	0·8349	1·0774
65	0·8293	1·0846
70	0·8238	1·0919
75	0·8181	1·0995
80	0·8129	1·1065

Decompositions.—1. Benzene may be heated in a close vessel to 200°, 300°, or 400° without alteration; but when passed through a porcelain tube heated to bright redness, it is partly decomposed, yielding hydrogen gas containing a little acetylene, and a liquid product separable by fractional distillation into: (1) Diphenyl, $C^{12}H^{10} = 2C^6H^6 - H^2$, distilling between 250° and 300°.—(2) Chrysene, $C^{18}H^{12} = 3C^6H^6 - 3H^2$, distilling above 360°.—(3) Benzerythrene, which distils at a dull red heat and solidifies into an orange-red resin of the consistence of colophony.—(4) A substance called by Berthelot bitumene, which remains in the retort at a dull red heat, as a blackish liquid, solidifying as it cools; it dissolves slightly in ether, forming a fluorescent liquid, which leaves on evaporation a film having a metallic lustre (Berthelot, *Bull. Soc. Chim.* [2] vi. 272, 279; *Jahresb.* 1866, p. 541).

2. Benzene heated in a glass tube over mercury with *acetylene* absorbs it, forming: (1) A small quantity of cinnamene, $C^8H^8 = C^6H^6 + C^2H^2$.—(2) A solid hydrocarbon, which, after the excess of benzene has been evaporated, remains in the form of slender needles, volatilising with difficulty.—(3) Tarry products.

3. A mixture of benzene and *ethylene* passed through a red-hot tube yields: (1) Cinnamene in considerable quantity at a red heat, and as chief product at a white heat.—(2) Naphthalene, the chief product at a red heat.—(3) Acenaphthene (p. 3), formed chiefly at a white heat.—(4) Anthracene mixed with a liquid hydrocarbon. The formation of cinnamene, naphthalene, and anthracene is represented by the equations

$$C^6H^6 + C^2H^4 = \underset{\text{Cinnamene.}}{C^8H^8} + H^2.$$

$$C^6H^6 + 2C^2H^4 = \underset{\text{Naphthalene.}}{C^{10}H^8} + 3H^2.$$

$$2C^6H^6 + C^2H^4 = \underset{\text{Naphthalene.}}{C^{14}H^{10}} + 3H^2.$$

4. Benzene and *marsh gas* do not act on one another under the same conditions as benzene and ethylene; but when they are brought together in the nascent state, as when a mixture of benzoate and acetate of sodium is subjected to dry distillation, they react so as to form toluene or methyl-benzene:

$$C^6H^6 + CH^4 = C^6H^5.CH^3 + H^2.$$

5. A mixture of benzene and *cinnamene* vapour passed through a red-hot tube yields anthracene, together with small quantities of naphthalene and a hydrocarbon resembling diphenyl:

$$\underset{\text{Cinnamene.}}{C^8H^8} + \underset{\text{Benzene.}}{C^6H^6} = \underset{\text{Anthracene.}}{C^{14}H^{10}} + 2H^2.$$

6. Benzene vapour and *naphthalene* vapour at a white heat yield anthracene:

$$C^{10}H^8 + 3C^6H^6 = 2C^{14}H^{10} + 3H^2$$

(Berthelot, *Bull. Soc. Chim.* [2] vii. 113, 274; *Jahresb.* 1866, p. 544).

7. Benzene oxidised by a mixture of *manganese dioxide* and sulphuric acid, is converted into formic, carbonic, benzoic, and phthalic acids (Carius, *Zeitschr. f. Chem.* iv. 505):

$$\underset{\text{Benzene.}}{C^6H^6} + \underset{\text{Formic acid.}}{H.CO^2H} + O = H^2O + \underset{\text{Benzoic acid.}}{C^6H^5.CO^2H}$$

and

$$\underset{\text{Benzoic acid.}}{C^6H^5.CO^2H} + \underset{\text{Formic acid.}}{H.CO^2H} + O = H^2O + \underset{\text{Phthalic acid.}}{C^6H^4(CO^2H)^2}$$

It is not attacked by potassium dichromate and sulphuric acid even after prolonged boiling (Church, *Phil. Mag.* [4] xxi. 176).

8. When 100 to 120 drops of benzene are taken into the stomach of men or dogs, the urine is found to contain phenol (Schultzen a. Naunyn, *Chem. Centr.* 1867, p. 705).—9. Benzene treated with *potassium chlorate* and *nitric acid* (sp. gr. 1·4) gives off a large quantity of gas, and yields a brownish oil which decomposes on distillation, yielding the compound $C^{12}H^{10}NO^2Cl$ or $\left.\begin{matrix}C^6H^5Cl\\C^6H^5NO^2\end{matrix}\right\}$, a volatile liquid smelling like bitter almond oil.—10. Heated for some time with *iodic acid* or *potassium iodate* and *sulphuric acid*, benzene yields phenyl iodide, C^6H^5I, together with a crystalline substance (H. Peltzer, *Ann. Ch. Pharm.* cxxxvi. 194).—11. Benzene heated to 150°

in sealed tubes with *sulphuric chloride*, SO^2Cl^2, is completely decomposed, yielding monochlorobenzene, hydrochloric acid, and sulphurous oxide:

$$C^6H^6 + SO^2Cl^2 = C^6H^5Cl + HCl + SO^2$$

(Dubois, *Zeitschr. f. Chem.* [2] ii. 705).

With *sulphuric chlorhydrate*, $SO^2.HO.Cl$, benzene yields sulphobenzide, together with smaller quantities of sulphobenzoic acid and sulphobenzoic chloride:

$$2C^6H^6 + SO^2.HO.Cl = \underset{\text{Sulphobenzide.}}{C^{12}H^{10}SO^2} + H^2O + HCl.$$

$$C^6H^6 + SO^2.HO.Cl = \underset{\substack{\text{Sulphobenzoic}\\ \text{acid.}}}{C^6H^5.SO^2OH} + HCl.$$

$$C^6H^6 + SO^2.HO.Cl = \underset{\substack{\text{Sulphobenzoic}\\ \text{chloride.}}}{C^6H^5SO^2Cl} + H^2O$$

(Knapp, *Zeitschr. f. Chem.* [2] v. 41;.

12. Benzene is not attacked by *alkalis* or by phosphorus pentachloride.—13. According to Lauth (*Bull. Soc. Chim.* [2] iv. 3), *sodium* attacks it with evolution of hydrogen and formation of a solid substance which encrusts the excess of sodium; but according to Berthelot, pure benzene is not attacked by sodium.

14. Benzene in the state of vapour unites with *carbonyl chloride*, forming benzoyl chloride (Harnitz-Harnitzky, *Ann. Ch. Pharm.* cxi. 192):

$$C^6H^6 + COCl^2 = HCl + C^6H^5.CO.Cl.$$

According to Berthelot, however (*Deut. Chem. Gesellsch.* 1869, p. 288; *Zeitschr. f. Chem.* [2] v. 480), pure carbonyl chloride does not act upon benzene (or upon ethylene or acetylene) either at ordinary or at higher temperatures; and when benzene is treated with ordinary phosgene gas (a mixture of carbonyl chloride with free chlorine), no benzoyl chloride is produced, the only action which takes place being due to the free chlorine.

On the other hand, Schützenberger finds (*Zeitschr. f. Chem.* [2] v. 631) that when benzene is acted upon by a mixture of sulphuric anhydride and carbon tetrachloride, which yields carbonyl chloride, ($2SO^3 + CCl^4 = S^2O^5Cl^2 + COCl^2$), and the product is heated with water, a considerable quantity of benzoic acid is obtained, together with hydrochloric acid, sulphobenzide, and benzene-sulphuric acid.

15. Benzene unites directly with 3 molecules of *hypochlorous acid*, forming the trichlorhydrin of phenose, $\left.\begin{matrix}(C^6H^6)^{vi}\\ H^3\end{matrix}\right\}\begin{matrix}O^3\\ Cl^3\end{matrix}$ (Carius, *Ann. Ch. Pharm.* cxxvi. 323). See PHENOSE.

16. Benzene agitated with aqueous *chlorous acid* is converted into trichlorophenomalic acid, $C^6H^7Cl^3O^5$:

$$C^6H^6 + 3HClO^2 = C^6H^7Cl^3O^5 + H^2O,$$

monochlorobenzene and dichloroquinone being formed at the same time (Carius, *Ann. Ch. Pharm.* cxlii. 129; *Jahresb.* 1866, p. 559). These last two products are formed in larger quantity when gaseous *chlorous anhydride* is made to act on dry benzene, $4C^6H^6 + 3Cl^2O^3 = 2C^6H^5Cl + 2C^6H^2Cl^2O^2 + 5H^2O$ (Carius, *Ann. Ch. Pharm.* cxliii. 315; *Bull. Soc. Chim.* [2] x. 49).

17. The method given by Hofmann (i. 542) for detecting the presence of benzene in a mixture of volatile oils has been modified as follows by Berthelot (*Bull. Soc. Chim.* [2] vi. 292), with the view of increasing its delicacy. A few drops of the liquid to be tested are mixed in a cooled tube with 4 times their volume of *fuming nitric acid*, and the mixture, after being briskly agitated and left to itself for a quarter of an hour, is mixed with ten times its bulk of water, which throws down drops of nitrobenzene. The whole is then agitated with an equal volume of common ether, which takes up the whole of the nitrobenzene. The ethereal solution is decanted, filtered, and rapidly distilled in a small retort to expel the ether. The drop of nitrobenzene remaining in the retort is then treated with 1 to 2 cubic centimetres of acetic acid and a particle of iron-filings, and distilled over a very small flame. As soon as the liquid in the retort is nearly evaporated, 2 or 3 cub. cent. of water are added, the distillation is repeated, and the distillates are mixed together. The liquid thus obtained is ready to be tested for aniline with chloride of lime. Sometimes, however, the presence of acetic acid interferes with the reaction. In that case a small piece of slaked lime is added, and the filtered liquid is placed in a porcelain capsule and treated with a dilute

aqueous solution of chloride of lime. By proceeding in this manner benzene may be detected in a cubic centimetre of a mixture containing not more than 2 per cent. of it.

18. With *chlorine* and *bromine*, benzene forms additive or substitution-products, according to the circumstances of the reaction. In sunshine additive compounds for the most part are obtained; but in diffused daylight only substitution-products are formed. Respecting the constitution of the additive compounds, see AROMATIC SERIES (p. 196).

BROMINATED DERIVATIVES OF BENZENE.

The *hexbromide* $C^6H^6Br^6$, produced by the action of bromine on benzene in sunshine, is described in vol. i. p. 543, under the name of *hydrobromate of tribromobenzene*, $C^6H^3Br^3.3HBr$.

Monobromobenzene. C^6H^5Br. Described at vol. i. p. 542, and iv. 414.—Griess has shown that it is produced in the decomposition of diazobenzene-platinobromide by caustic soda, according to the equation $2(C^6H^4N^2.HBr).PtBr^4 = 2C^6H^5Br + Pt + 2Br^2 + 2N^2$; also by heating diazobenzene-perbromide with sodium carbonate, or by warming its alcoholic solution, $C^6H^4N^2.HBr^3 = C^6H^5Br + N^2 + Br^2$ (see iv. 331). Heated for several days with *ethyl chlorocarbonate* and *sodium amalgam*, it yields ethyl benzoate (Wurtz, *Zeitschr. f. Chem.* [2] iv. 385):

$$C^6H^5Br + CO\begin{cases}OC^2H^5\\Cl\end{cases} + Na^2 = NaCl + NaBr + C^6H^5.CO^2(C^2H^5).$$

Dibromobenzene, $C^6H^4Br^2$ (i. 543; iv. 414), may be obtained, together with the tetrabrominated compound, by distilling monobromophenol with phosphorus pentabromide: $C^6H^5BrO + PBr^5 = C^6H^4Br^2 + HBr + POBr^3$ (A. Mayer, *Ann. Ch. Pharm.* cxxxvii. 210). According to Friedel (*Bull. Soc. Chim.* [2] xi. 38), the crystals (obtained by Couper) are oblique rhomboïdal prisms, isomorphous with those of dichlorobenzene. F. Riese (*Berlin. Chem. Gesellsch.* 1869, p. 60) in preparing ordinary (*α*) dibromobenzene, obtained a small quantity of a liquid modification (*β*). This modification solidifies below 0°, melts at $-1°$, and boils without decomposition at 214°, whereas *α*-dibromobenzene melts at 89°, and boils at 219°. By solution in fuming nitric acid and precipitation with water, a *β*-nitrodibromobenzene is obtained, which forms needles melting at 58° (*α*-nitrodibromobenzene melts at 84°). Sodium acts slowly on *α*-dibromobenzene, producing brominated compounds, diphenyl, and a hydrocarbon boiling above 360° but below the boiling point of sulphur.

Tribromobenzene, $C^6H^3Br^3$, is obtained: (*α*) By treating the hexbromide $C^6H^6Br^6$ with boiling alcoholic potash (i. 543).—(*β*) By treating dibromobenzene with bromine.—(*γ*) By the action of phosphorus pentabromide on dibromophenol (Mayer). It crystallises in tufts of white shining needles; sublimes at about 50° in highly lustrous needles; melts at 44°, and distils between 266° and 280°, the greater part passing over at 275°. It is soluble in alcohol and ether. By strong nitric acid it is converted into mononitro-tribromobenzene, and by a hot mixture of nitric and sulphuric acids into dinitro-tribromobenzene (Mayer).

Tetrabromobenzene, $C^6H^2Br^4$, exists in two modifications, one of which, obtained by heating the preceding compound with bromine, has been already described (iv. 415); it melts at 160° (Riche a. Bérard); at 137°–140° (Kekulé, *Ann. Ch. Pharm.* cxxxvii. 72). The other modification is obtained by the action of phosphorus pentabromide on tribromophenol. It forms shining needles melting at 95° (Körner); at 98° (Mayer); and, like the preceding, yields a crystallised nitro-derivative.

Pentabromobenzene, C^6HBr^5, is produced in small quantity, together with tetrabromobenzene, by heating nitrobenzene or dinitrobenzene with bromine to 250°. It crystallises in silky needles fusible and volatile without decomposition; its melting point is above 240°. Nearly soluble in cold, slightly soluble in boiling alcohol; dissolves easily in benzene or in a mixture of benzene and alcohol.

CHLORINATED DERIVATIVES OF BENZENE.

I. *Additive Compounds.*

Benzene Hexchloride, $C^6H^6Cl^6$, described at p. 543, vol. i., as *hydrochlorate of trichlorobenzene*, is produced by the action of chlorine in sunshine under the influence of the direct solar rays. According to Berthelot, the formation of this crystalline body affords a test of the purity of the benzene, as with impure benzene the crystals are not produced. According to Lesimple (*Bull. Soc. Chim.* [2] vi. 161), the compound is easily obtained by passing chlorine into the vapour of benzene [in sunshine?].

Chlorides of Chlorinated Benzenes. These compounds are produced by the action of chlorine in sunshine on monochlorobenzene and on sulphobenzide.

a. When monochlorobenzene is introduced into a flask of colourless glass filled with dry chlorine and exposed to the sun's rays, the flask becomes hot and filled with white vapours, and the chlorine is rapidly absorbed. If the chlorobenzene is in excess, the gas disappears completely, and a thick oil is produced; but if the chlorine is in excess, hydrochloric acid is formed, and a crystalline body makes its appearance, together with the oil. In the former case the product consists of a mixture of the four compounds

$$C^6H^4Cl.Cl^2, \quad C^6H^5Cl.Cl^4, \quad C^6H^4Cl.Cl^6, \quad C^6H^5Cl.Cl^6;$$

in the latter, of these same compounds, together with others formed from them by replacement of 1 at. hydrogen with chlorine, namely, $C^6(H^4Cl)Cl.Cl^2$, &c. The oil drained from the crystals is partly decomposed by distillation into hydrochloric acid and chlorinated benzenes: e.g. $C^6H^5Cl.Cl^2$ into HCl and $C^6H^4Cl^2$. The same decomposition is completely effected by heating with alcoholic potash. The resulting alcoholic solution mixed with water deposits a heavy oil mixed with crystals; and on washing this oil with water, drying it, and submitting it to repeated fractional distillation, there are obtained (besides a large quantity of unattacked monochlorobenzene passing over at 140°): *dichlorobenzene*, distilling at about 175°; *trichlorobenzene*, at 210°; *tetrachlorobenzene*, at 245°; *pentachlorobenzene*, at 275°; and at a higher temperature a mixture of the latter with *hexchlorobenzene* (Jungfleisch, *Bull. Soc. Chim.* [2] ix. 346; *Zeitschr. f. Chem.* [2] iv. 484).

The crystals obtained as above described when the chlorine is in excess consist chiefly of dichlorobenzene hexchloride, $C^6H^4Cl^8 = C^6H^4Cl^2.Cl^6$; and by separating them from the oily product, washing them with cold alcohol, and recrystallising several times from chloroform, this compound is obtained in colourless, well-defined, oblique rhomboïdal prisms. Heated with alcoholic potash, it yields potassium chloride and pentachlorobenzene, melting at 74°, and identical with that which is produced by direct substitution (p. 266).

β. When sulphobenzide is exposed to the action of dry chlorine in sunshine, a thick yellowish oil is formed, and by prolonged action, also a crystalline body, which covers the sides of the retort and receiver. The oil is a mixture of chlorinated compounds, containing a portion of the crystalline compound in solution, and when decomposed by alcoholic potash yields a mixture of chlorinated benzenes, chiefly $C^6H^4Cl^2$ and C^6HCl^5. The crystalline body, after separation from the oil by filtration through asbestos, washing with ether, pressing, and recrystallisation from boiling absolute alcohol, forms small quadratic prisms, having a vitreous lustre, melting between 255° and 257°, sublimable without decomposition, insoluble in water, slightly soluble in cold alcohol and ether, very soluble in hot alcohol. Alcoholic potash decomposes them, with formation of potassium chloride. The analysis of these crystals leads to the formula $C^6H^5Cl^7$, which is that of monochlorobenzene-hexchloride, $C^6H^5Cl.Cl^6$ (Otto a. Ostrop, *Ann. Ch. Pharm.* cxli. 105; *Jahresb.* 1866, p. 573). Jungfleisch, on the other hand, regards them as identical with dichlorobenzene hexchloride, $C^6H^4Cl^2.Cl^6$, and this view has been confirmed by subsequent experiments of Otto (*Zeitschr. f. Chem.* [2] vi. 36). When heated with potash they are converted into pentachlorobenzene, melting at 85°: $C^6H^4Cl^2.Cl^6 = 3HCl + C^6HCl^5$ (Otto).

II. *Substitution-products. Chlorobenzenes.*

There are two general methods of preparing these compounds: *a.* By passing chlorine into benzene containing iodine (Hugo Müller, iv. 414; Jungfleisch, *Ann. Ch. Phys.* [4] xv. 186–329; *Jahresb.* 1867, pp. 342–355).—*β.* By heating the additive compounds above described with alcoholic potash (Jungfleisch, *Ann. Ch. Phys.* [4] xv. 291; *Jahresb.* 1867, p. 355). The monochlorinated compound is the same, whether obtained by the one or the other process; but, according to Jungfleisch, the di-, tri-, tetra-, and pentachlorobenzenes obtained by the second process are not identical, but only isomeric, with those obtained by direct substitution. The existence of two isomeric modifications of the di-, tri-, and tetra-chlorinated compounds is easily explained on Kekulé's view of the constitution of benzene, by the different relative positions of the chlorine-atoms; they are, in fact, susceptible of three such modifications; but the existence of two pentachlorobenzenes, if established, requires that theory to be modified in the manner suggested by Städeler. (See AROMATIC SERIES, p. 194.)

Lesimple (*Zeitschr. f. Chem.* [2] iv. 235) recommends dry antimony trichloride as the best vehicle of chlorine for the preparation of these compounds; it dissolves easily in benzene with aid of heat, and may afterwards be completely removed by hydrochloric acid.

Monochlorobenzene. C^6H^5Cl.—1. In preparing this compound by passing chlorine into benzene containing iodine (iv. 414), Jungfleisch finds it advantageous to distil the liquid from time to time, in order to withdraw the portion boiling above 130° from the further action of the chlorine. The crude chlorobenzene (also containing iodobenzene) is purified by alternate agitation with potassium hydrate and exposure for several days to sunshine, and finally by fractional distillation.—2. The same compound is obtained by the action of phosphorus pentachloride on phenol (iv. 414); see also Glutz (*Ann. Ch. Pharm.* cxliii. 181; *Jahresb.* 1867, p. 607).—3. Together with chloride of sulphobenzene, by the action of chlorine in diffused daylight at 120°–130°, or of phosphorus pentachloride, on sulphobenzide (Otto, *Ann. Ch. Pharm.* cxxxvi. 154; Otto a. Ostrop, *ibid.* cxli. 93):

$$\underset{\text{Sulphobenzide.}}{(C^6H^5)^2SO^2} + Cl^2 = \underset{\text{Chlorobenzene.}}{C^6H^5Cl} + \underset{\text{Sulphobenzene chloride.}}{C^6H^5SO^2Cl}$$

$$(C^6H^5)^2SO^2 + PCl^5 = C^6H^5Cl + C^6H^5SO^2Cl + PCl^3.$$

When chlorine acts on sulphobenzide in direct sunshine, part of the chlorobenzene produced takes up 2 at. chlorine, forming the crystalline compound above described.—4. By heating diazobenzene-platinochloride with sodium carbonate (Griess, iv. 432).—5. By the action of chlorous anhydride on benzene (Carius, p. 262).

Monochlorobenzene (prepared by 1) boils at 138°, is indifferent to alcoholic potash, and is not attacked by zinc or tin, even at 140°; with an alloy of tin and sodium it yields a white pulverulent body, soluble in alcohol, and converted by nitric acid into nitrobenzene and stannic oxide (Jungfleisch). According to Sokoloff (*Jahresb.* 1865, p. 517; 1866, p. 551), the action of phosphorus pentachloride on phenol yields a compound (phenyl chloride) differing in its properties from the monochlorobenzene obtained by the action of iodine chloride on benzene; thus phenyl chloride has a sp. gr. of 1·1199 at 0° and 1·092 at 30°, and boils at 136° (bar. at 0·767 met.), whereas chlorobenzene has a sp. gr. of 1·499 at 0° and 1·1188 at 30°, and boils at 132·5°. Moreover, nitric acid acts more rapidly on the former than on the latter, though the products of the reaction are the same in both cases. These differences are, however, not of sufficient magnitude to warrant the conclusion that the monochlorobenzenes produced by the two processes are merely isomeric and not identical.

Monochlorobenzene treated with *sulphuric anhydride* is converted into dichlorosulphobenzide and sulphochlorobenzolic acid:

$$\underset{\text{Chlorobenzene.}}{3C^6H^5Cl} + 2SO^3 = \underset{\text{Dichlorosulphobenzide.}}{\left.\begin{matrix} C^6H^4ClSO^2 \\ C^6H^4Cl \end{matrix}\right\}} + \underset{\text{Sulphochlorobenzolic acid.}}{C^6H^5ClSO^3} + H^2O$$

(Otto, *Ann. Ch. Pharm.* cxlv. 28).

By the gradual action of a mixture of *manganese dioxide* and *dilute sulphuric acid*, chlorobenzene is converted into parachlorobenzoic acid, in the same manner as benzene into benzoic acid (p. 261):

$$C^6H^5Br + CH^2O^2 + O = H^2O + C^6H^4Cl.CO^2H$$

(Carius, *Zeitschr. f. Chem.* [2] iv. 505; C. Müller, *ibid.* v. 137).

Dichlorobenzene. $C^6H^4Cl^2$ (H. Müller, *Zeitschr. f. Chem.* 1864, p. 401; Jungfleisch, *loc. cit.*).—This compound is prepared by passing chlorine into a solution of iodine in benzene, till the liquid partly solidifies in the crystalline state on cooling, and again subjecting the liquid drained from the crystals to the action of chlorine. The crystals are washed with a cold-saturated alcoholic solution of dichlorobenzene, then decolorised by washing with alkaline water, and finally crystallised from alcohol or ether. It forms, especially after very slow evaporation of the ethereal solution, large right rhombic prisms, which melt at 53° and boil at 171° (Jungfleisch); 172° (Müller). According to Müller, it sublimes in closed vessels, even at ordinary temperatures, in large four-sided prisms. Sp. gr. 1·46 at 20°. Insoluble in water, easily soluble in alcohol and ether, not decomposed by sulphuric acid or alcoholic potash. With fuming nitric acid it forms two nitro-compounds, one of which forms distinct crystals. In ethereal solution it is decomposed by sodium or sodium-amalgam, without evolution of gas. The dichlorobenzene which Griess obtained by decomposition of the platinum salt of diazochlorobenzene (iv. 415) appears to be identical with that just described. Another modification, melting below 0°, and distilling at 175°, is formed, together with other products, by the action of alcoholic potash on the oily product of the action of chlorine on monochlorobenzene in sunshine, apparently by abstraction of HCl from the compound $C^6H^5Cl.Cl^2$ (Jungfleisch).

Trichlorobenzene, $C^6H^3Cl^3$, is known in two modifications, one being that which Mitscherlich obtained (i. 543) by decomposing the compound $C^6H^6Cl^6$ with alcoholic potash. According to Jungfleisch, the same modification is formed by the action of iodine chloride on benzene, and may be separated from the other products of this reaction by submitting the liquid drained from the crystals of dichlorobenzene to fractional distillation, collecting the portion which boils above 215°, and freeing it from the more easily crystallisable products by cooling. The trichlorobenzene thus obtained melts at 16° or 17°, and boils at 206°, whereas Mitscherlich's product remained liquid below 0° and boiled at 210°. Nevertheless, Jungfleisch regards his product as identical with Mitscherlich's, since the nitro-compounds obtained from the two are identical in every respect; he attributes the different physical properties of Mitscherlich's compound to impurities, inasmuch as, in the action of potash on the compound $C^6H^6Cl^6$, other compounds, especially chlorinated phenols, are simultaneously produced. The same modification of trichlorobenzene is found among the products obtained by decomposing with alcoholic potash the oily product of the action of chlorine on monochlorobenzene, together with another, which is crystalline at ordinary temperatures, and melts at 60° (Jungfleisch).

Tetrachlorobenzene. $C^6H^2Cl^4$.—Of this compound also two modifications are known, both crystalline at ordinary temperatures. One of them is obtained by the action of chlorine on benzene containing iodine, and separates on cooling from the fraction of the distillate boiling above 220°. For purification it is washed with potash, crystallised from alcohol, subjected to fractional distillation, to free it from the pentachlorinated compound, and finally recrystallised. It forms long, white, silky crystals, melting at 139°, and boiling without decomposition at 240°. Insoluble in water, easily soluble in hot alcohol and in ether, not decomposed by sulphuric acid, but convertible by fuming nitric acid into a crystalline nitro-compound (Jungfleisch). This modification is also obtained, as a secondary product, in the preparation of trichlorobenzyl trichloride, $C^6H^2Cl^3.CCl^3$, from trichlorotoluene, $C^6H^2Cl^3.CH^3$ (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2] v. 529). The other modification is obtained in considerable quantity by the action of alcoholic potash on the oil obtained by the action of chlorine on monochlorobenzene (p. 264); it passes over nearly pure between 245° and 250°, and is easily rendered quite pure by a few recrystallisations from alcohol (Jungfleisch). The same modification is obtained (together with other chlorobenzenes) by the action of alcoholic potash on the yellow oil which is formed, together with hexchloride of monochlorobenzene (p. 263), by the action of chlorine on sulphobenzide. The tetrachlorobenzene is contained in the portion of the product which on fractional distillation passes over between 250° and 260° (Otto a. Ostrop). This modification crystallises in long, colourless nacreous needles; melts at 35°; boils at 253°; dissolves easily in boiling, less easily in cold alcohol; is soluble also in ether, benzene, chloroform, and carbon bisulphide. Antimonic chloride converts it into hexchlorobenzene (Jungfleisch).

Pentachlorobenzene, C^6HCl^5, is contained in that portion of the liquid produced by the action of iodine chloride on benzene, which distils at about 275°; it crystallises easily in stellate groups of needles, melting at 74°, and boiling at 272° (Jungfleisch). The same compound, in two modifications, constitutes that portion of the product of the action of alcoholic potash on the oil obtained by treating monochlorobenzene with chlorine (p. 263), which passes over at about 270°, and in larger quantity than any of the other distillates. The crystalline mass thus obtained may be separated into the two modifications of pentachlorobenzene by fusing it and treating it with boiling alcohol, which dissolves the modification above described, and leaves the other in the form of powder. The first modification may be obtained perfectly pure by recrystallisation from alcohol, and the second from a mixture of alcohol and benzene. The latter crystallises in very slender silky crystals, nearly insoluble in alcohol and in ether, soluble in benzene and in chloroform. The crystals melt at 175°, if brought directly into a bath heated to this temperature, but after solidification they do not fuse below 198°; they melt also at nearly the same temperature if the heat of the bath be slowly raised (Jungfleisch, *Jahresb.* 1868, p. 357). The same modification is found among the products of the action of alcoholic potash on the oil obtained by treating sulphobenzide with chlorine (Otto a. Ostrop; see further, Otto, *Zeitschr. f. Chem.* [2] vi. 25). See p. 264, also AROMATIC SERIES (p. 194).

According to Beilstein a. Kuhlberg (*Zeitschr. f. Chem.* [2] v. 529), the first modification is likewise obtained, in an impure state, by passing chlorine into tetrachlorobenzyl chloride, $C^6HCl^4.CH^2Cl$, at the boiling heat. Both modifications are converted by antimonic chloride into hexchlorobenzene.

Hexchlorobenzene, C^6Cl^6, is obtained: 1. By pouring benzene on antimonic chloride and passing chlorine into the liquid as long as it is absorbed. The antimony chloride is then removed by hydrochloric acid, and the hexchlorobenzene is purified by crystallisation or sublimation (H. Müller, *Zeitschr. Ch. Pharm.* 1864, p. 40).—2. It is present in small quantity amongst the highest products of the action of alcoholic potash on the oil resulting from the action of chlorine on monochlorobenzene (Jungfleisch, p. 263).—3. By the action of phosphorus pentachloride on tetrachloroquinone, tetrachlorhydroquinone, and trichloroquinone:

$$\underset{\text{Tetrachloroquinone.}}{C^6Cl^4O^2} + 2PCl^5 = C^6Cl^6 + 2POCl^3 + Cl^2$$

$$\underset{\text{Tetrachlorhydroquinone.}}{C^6H^2Cl^4O^2} + 2PCl^5 = C^6Cl^6 + 2POCl^3 + 2HCl$$

$$\underset{\text{Trichloroquinone.}}{C^6HCl^3O^2} + 2PCl^5 = C^6Cl^6 + 2POCl^3 + HCl;$$

also, together with pentachlorobenzene, by the action of phosphorus pentachloride on trichlorhydroquinone (C. Graebe, *Ann. Ch. Pharm.* cxlvi. 1; *Jahresb.* 1867, p. 651).—4. According to Beilstein a. Kuhlberg (*Zeitschr. f. Chem.* [2] v. 183), it is the ultimate product of the action of antimonic chloride, $SbCl^5$, on all chlorotoluenes and chloroxylenes. It crystallises in fine silky prismatic needles of a dazzling whiteness; melts at 220°; begins to sublime at a lower temperature; is insoluble in water, slightly soluble in cold alcohol, easily in boiling alcohol, ether, and benzene; is with difficulty attacked by potash, not at all by nitric acid (Müller). It is identical with Julin's chloride of carbon produced by the decomposition of chloroform vapour at a bright red heat. According to Berthelot a. Jungfleisch (*Zeitschr. f. Chem.* [2] iv. 565), hexchlorobenzene melts at 226° and boils at 326° (corr.); Julin's chloride of carbon melts at 226° and boils at 331° (corr.). Both dissolve to very nearly the same extent in carbon bisulphide at corresponding temperatures. Moreover, the vapour-density of the compound prepared from chloroform was found by Bassett (*Chem. Soc. J.* [2] v. 243) to be 10·06, and the density calculated for the formula C^6Cl^6 is 9·87.

IODOBENZENES.

Mono-iodobenzene, C^6H^5I, originally obtained by the action of iodine and phosphorus on phenol (Scrugham, iv. 415), is likewise produced: *a.* In the decomposition of iodine-benzoate, or in the action of iodine chloride on sodium benzoate (Schützenberger, *Compt. rend.* lii. 963). See BENZOATES.—*β.* By heating benzene for some time with iodic acid, or with potassium iodate and sulphuric acid (Peltzer, *Ann. Ch. Pharm.* cxxxv. 194).—*γ.* By the action of hydriodic acid on diazobenzene: $C^6H^4N^2 + HI = C^6H^5I + N^2$ (Griess).—*δ.* By the action of iodine and iodic acid on benzene. A mixture of 20 grms. benzene, 15 grms. iodine, and 10 grms. iodic acid is heated in sealed tubes to 200°–240°, the tubes being opened from time to time to give vent to carbon dioxide resulting from a secondary action. The product is distilled, either immediately or after washing with water and alkali, the mono-iodobenzene then passing over between 180° and 190°, while di-, and sometimes also tri-iodobenzene remains behind (Kekulé, *Ann. Ch. Pharm.* cxxxvii. 157).

Mono-iodobenzene, when purified by repeated rectification, is a colourless liquid, insoluble in water, smelling like benzene and phenol. It does not solidify at −18°; boils at 185°; has a sp. gr. of 1·69 (Schützenberger) 1·833 at 15° (Kekulé). By sodium-amalgam and water it is easily reconverted into benzene, also by aqueous hydriodic acid at 250°. It is not decomposed by solid potassium hydrate, or by the alcoholic solution of potash or ammonia (Kekulé).

Di-iodobenzene, $C^6H^4I^2$, is likewise produced in the decomposition of iodine-benzoate by heat (Schützenberger), and by the action of iodine and iodic acid on mono-iodobenzene (or the crude product of its preparation). On distilling the washed product, liquid mono-iodobenzene passes over first, while the following crystallisable portion contains di- and tri-iodobenzene (the former greatly predominating) which may be separated, though with difficulty, by crystallisation from alcohol (Kekulé).

Di-iodobenzene forms white nacreous laminæ resembling naphthalene, melting at 122° (Sch.), at 127° (K.), boiling at 250° (Sch.), at 277 (corr. 285°) (Kekulé), and subliming at comparatively low temperatures.

Tri-iodobenzene, $C^6H^3I^3$, forms small needles, melting at 76° and subliming without decomposition (Kekulé).

NITROBENZENES.

Mononitrobenzene. $C^6H^5(NO^2)$.—Schiff (*Ann. Ch. Pharm.* cxiv. 201) has found this compound amongst the products of the action of strong nitric acid on turpentine-oil. These products evaporated at a gentle heat, mixed with sand and distilled, yield a strongly acid watery liquid, and a brown oil containing nitrobenzene.

Nitrobenzene is prepared on the large scale, for the manufacture of aniline, by treating benzene, either with a mixture of sodium nitrate and sulphuric acid, or with a mixture of ordinary nitric acid of sp. gr. 1·3 and strong sulphuric acid. The apparatus used consists of large cast-iron pots provided with stirrers. (See Perkin's 'Lectures on Aniline Colours,' *Journal of the Society of Arts.*)

Reactions.—Nitrobenzene is converted, by oxidation with potassium dichromate and sulphuric acid, into nitrophenoic acid, $C^6H^3(NO^2)O^2$ (Church, iv. 388).

Most of the reagents employed for the reduction of nitrobenzene to aniline are mentioned under PHENYLAMINE (iv. 420). The reduction may also be effected by heating with *carbon bisulphide* to 160° (Schlagdenhauffen, *J. Pharm.* [3] xxxiv. 175); by heating it to 104° with *hydriodic acid* of sp. gr. 1·44 (E. J. Mills, *Jahresb.* 1864, p. 525); and by means of *tin* and *hydrochloric* acid, operating, however, only with small quantities, as the reaction is very violent (Scheurer-Kestner, *Rép. Chim. app.* iv. 121).

Heated in sealed tubes with *hydrobromic acid* to 185°–190°, nitrobenzene yields mono- and di-bromaniline. The reduction takes place in the same way as with hydriodic acid, viz.,

$$C^6H^5NO^2 + 6HBr = C^6H^5NH^2 + 3Br^2 + 2H^2O,$$

the difference in the products arising merely from the circumstance that bromine exerts a substituting action upon aniline salts, whereas iodine does not (H. Baumhauer, *Zeitschr. f. Chem.* [2] v. 198). With *hydrochloric acid* in like manner to 245° it yields dichloraniline, with a small quantity of aniline (Baumhauer, *ibid.* vi. 8).

With *iron-filings* and *hydrochloric acid* nitrobenzene yields a red colouring matter called erythrobenzin (F. Laurent a. J. Castlehaz, *Jahresb.* 1862, p. 693).

Nitrobenzene in alcoholic solution is reduced by *sodium-amalgam* to azoxybenzene, $C^{12}H^{10}N^2O$, or, if the sodium-amalgam is in excess, into azobenzene, $C^{12}H^{10}N^2$, which by further action is converted into hydrazobenzene, $C^{12}H^{12}N^2$. Exactly the same reactions are produced by zinc-dust in presence of a small quantity of potash or soda (Alexeyeff, *Bull. Soc. Chim.* [2] i. 324; *Zeitschr. f. Chem.* [3] iii. 33).

Nitrobenzene dissolved in dilute alcohol and boiled with 3 mol. *ammonium sulphite* is converted into disulphanilic acid, $C^6H^{13}NS^2O^6$ (Carius, *Jahresb.* 1861, p. 634):

$$C^6H^5NO^2 + 3(NH^4)^2SO^3 = C^6H^{13}NS^2O^6 + (NH^4)^2SO^4 + H^2O + 2NH^3.$$

Di-nitrobenzene, $C^6H^4(NO^2)^2$, is reduced by *iron* and *acetic acid* to phenylene-diamine, $C^6H^8N^2$ (Hofmann, *Proc. Roy. Soc.* xi. 518). A mixture of dinitrobenzene (1 mol.) and metallic tin (6 at.) dissolves rapidly in strong hydrochloric acid, forming a liquid which on evaporation deposits a double salt of phenylene-diamine hydrochloride with stannous chloride, $C^6H^8N^2.2HCl.2SnCl^2$, in needles having a silky lustre (H. Gerdemann, *Jahresb.* 1865, p. 412).

In the reduction of nitro-compounds by *tin* and *hydrochloric acid*, it is to be observed: (1) that the reaction does not necessarily stop at the formation of stannous chloride, but may proceed to the formation of stannic chloride, inasmuch as many nitro-compounds are reduced by stannous chloride (nitrobenzene, for example, with violence); and (2) that the result depends also upon the nature of the solvent and the solubility therein of the nitro-compound and of any possible intermediate product of reduction. Thus when di-nitrobenzene is treated with tin and *aqueous* hydrochloric acid, in which it is insoluble, whereas the intermediate product of reduction (para-nitraniline) is soluble, then even if the nitro-compound is in excess, the final product, paraphenylene-diamine, is formed, chiefly or exclusively, together with stannic chloride, and the excess of dinitrobenzene remains unattacked, because the soluble intermediate product formed in the first instance is exposed to the full action of the reducing agent. But if an alcoholic solution of dinitrobenzene is used, and the tin added in the quantity required for the formation of stannic chloride, then on passing hydrochloric acid gas into the liquid, only paranitraniline is produced (Kekulé, *Zeitschr. f. Chem.* [2] ii. 695).

Nitrobromobenzenes. The compounds $C^6H^4(NO^2)Br$ and $C^6H^3(NO^2)Br^2$ have been already described (iv. 416).

Dinitrobromobenzene, $C^6H^3(NO^2)^2Br$, produced by heating monobromobenzene with a mixture of fuming nitric acid and sulphuric acid, crystallises in large yellow transparent prisms, melting at 72°, soluble in boiling alcohol (Kekulé, *Ann. Ch. Pharm.* cxxxvii. 129).

Nitrotribromobenzene, $C^6H^2(NO^2)Br^3$, obtained by treating tribromobenzene with fuming nitric acid, precipitating with water, and crystallising from hot alcohol, forms long yellow needles, sparingly soluble in cold, easily soluble in hot alcohol, also in ether, benzene, and carbon bisulphide (A. Mayer, *Ann. Ch. Pharm.* cxxxvii. 219).

Dinitrotribromobenzene, $C^6H(NO^2)^2Br^3$, is produced (together with a little bromopicrin) by heating the preceding compound with a mixture of fuming sulphuric and nitric acids. It dissolves easily in hot alcohol, ether, benzene, and carbon bisulphide, and crystallises from the latter in yellowish scales melting at 125° (Mayer, *loc. cit.*).

Nitrotetrabromobenzene, $C^6H(NO^2)Br^4$, produced by the action of fuming nitric acid on tetrabromobenzene, is white, crystalline, melts at 88°, sublimes in flocks, and dissolves sparingly in cold, more freely in hot alcohol and ether (Riche a. Bérard; Mayer).

Nitrochlorobenzenes. *Nitrochlorobenzene*, $C^6H^4(NO^2)Cl$, has been already described (i. 416) as a crystalline body produced by treating monochlorobenzene with fuming nitric acid. According to Sokoloff (*Jahresb.* 1866, p. 551) and Lesimple (*Zeitschr. f. Chem.* [2] iv. 225), an oily modification of the compound is formed at the same time.

Nitrodichlorobenzene, $C^6H^3(NO^2)Cl^2$, produced by treating dichlorobenzene with fuming nitric acid, crystallises from alcohol in thin plates, insoluble in water, slightly soluble in cold alcohol, more freely in ether, benzene, and hot alcohol. Melts at 55°, distils without decomposition when strongly heated, and smells like cinnamon. An oily modification appears to be formed simultaneously with this crystalline body (Lesimple, *Zeitschr. f. Chem.* [2] iv. 226; see also Jungfleisch, *Bull. Soc. Chim.* [2] iv. 241).

Nitrotrichlorobenzene, $C^6H^2(NO^2)Cl^3$, produced by the action of fuming nitric acid at the boiling heat on trichlorobenzene, crystallises in colourless needles melting below 100°. It boils without decomposition at 273·5°, is insoluble in water, slightly soluble in cold alcohol, freely in boiling alcohol, ether, and benzene. Treated in alcoholic solution with zinc and hydrochloric acid, it is converted into trichloraniline (Lesimple, *Bull. Soc. Chim.* [2] vi. 161).

Nitrotetrachlorobenzene, $C^6H(NO^2)Cl^4$, is a crystallisable compound, formed by heating tetrachlorobenzene with fuming nitric acid (Jungfleisch), or by repeated treatment with a mixture of fuming nitric and sulphuric acids, and even then with difficulty. Crystallises from hot alcohol in needles, absolutely insoluble in water, and very sparingly soluble in most alcoholic solvents. Melts at 75°–78°, solidifies at 62°, and distils at about 300° (Lesimple).*

Nitro-iodobenzene, $C^6H^4(NO^2)I$, is known in two modifications: the one, produced by the action of iodine monochloride on sodium nitrobenzoate, is a yellow liquid having a distinct odour of bitter almonds, and boiling at about 290° (Schützenberger a. Segenwald, *Rép. Chim. pure*, 1862, p. 144). The other, produced by the action of fuming nitric acid on mono-iodobenzene, crystallises in beautiful pale yellow needles, melting at 171°, and subliming without decomposition (Kekulé, *Ann. Ch. Pharm.* cxxxvii. 129).

COMPOUNDS FORMED BY REDUCTION OF THE NITROBENZENES.

Respecting amidobenzene, $C^6H^5(NH^2)$, diamidobenzene, $C^6H^4(NH^2)^2$, and their derivatives, see PHENYLAMINES and PHENYLENE-DIAMINES (iv. 419–484); also the same articles and ANILINE in this volume.

The diazobenzenes and diazo-amidobenzenes are described under AZO-PHENYLAMINES and AZODIPHENYL-DIAMINES (iv. 430, 459).

Azobenzene. $C^{12}H^{10}N^2$.—This compound is formed by the action of sodium-amalgam on an alcoholic solution of nitrobenzene acidulated with acetic acid (Werigo, *Ann. Ch. Pharm.* cxxxv. 176). According to Alexejeff (*Zeitschr. f. Chem.* [2] iii. 33), the product of this reaction is azoxybenzene or azobenzene, accordingly as the nitrobenzene or the sodium-amalgam is in excess; in the latter cases the azobenzene is converted, by prolonged action of the sodium-amalgam, into hydrazobenzene, $C^{12}H^{12}N^2$. Exactly the same effects are produced by zinc-dust, with addition of a small quantity of potash or soda (Alexejeff, *Zeitschr. f. Chem.* [2] iv. 497).

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* Further details on the nitrochlorobenzenes, according to the latest investigation of Jungfleisch, will be given under N.

Azobenzene is also produced, together with azoxybenzene and hydrazobenzene, by oxidation of aniline with solution of potassium permanganate. Manganic oxide is thereby separated, carrying down with it the greater part of the azo-compounds produced. The precipitate washed with cold water yields, on distillation in the water-bath, red drops of azobenzene which solidify on cooling. The azobenzene may also be extracted from the precipitate by hot alcohol; the mother-liquor, from the first crystallisation of the azobenzene, often yields lighter-coloured needles of azoxybenzene; and on distilling the crude product, quadratic laminæ were once observed, which exhibited the reactions of hydrazobenzene. The formation of azobenzene from aniline is represented by the equation

$$2C^6H^7N + O^2 = C^{12}H^{10}N^2 + 2H^2O$$

(E. Glaser, *Ann. Ch. Pharm.* cxlii. 364). Respecting the constitution of these bodies, and their relation to nitrobenzene and aniline, see AROMATIC SERIES (pp. 208–210).

In the action of reducing agents on azobenzene, the latter is in the first instance converted into hydrazobenzene, afterwards into the isomeric and more stable compound benzidine (Hofmann, *Proc. Roy. Soc.* xii. 576).

A mixture of 1 mol. azobenzene with 2 mols. *aniline hydrochloride* heated to 170°–230° in closed vessels, yields a blue and a violet colouring matter. 1 mol. azobenzene and 1 mol. *toluidine hydrochloride* yield, in like manner, violet and blue substances, together with a small quantity of a product having a fine ruby colour (Städeler, *J. pr. Chem.* xcvi. 65; *Jahresb.* 1865, p. 409).

Azobenzene unites directly with 2 at. *bromine*, forming the compound $C^{12}H^{10}N^2Br^2$, which is slightly soluble in alcohol and ether, and crystallises in golden-yellow needles melting at 205°, and subliming in large iridescent needles. This compound is isomeric with dibromobenzidine. It dissolves in hot strong sulphuric acid, and is converted by fuming nitric acid into the compound $C^{12}H^9(NO^2)N^2Br^2$ melting at 150° (Werigo, *Ann. Ch. Pharm.* cxxxv. 176).

Azobenzene heated with strong *hydrobromic acid* is converted into a white crystalline body, forming with water a solution from which sodium hydrate throws down an oil, quickly solidifying in the crystalline form (Werigo, *Zeitschr. f. Chem.* [2] iv. 210).

Azobenzene-sulphuric acid, $C^{12}H^{10}N^2SO^3$, is produced by heating azobenzene with fuming sulphuric acid to 150°. It forms yellow crystals or red scales, and yields crystallisable salts. The silver salt contains $C^{12}H^9AgN^2SO^3$ (Griess, *Ann. Ch. Pharm.* cxviii. 89).

AMIDAZOBENZENE OR AMIDODIPHENYLIMIDE. $C^{12}H^{11}N^3 = C^{12}H^9(NH^2)N^2$ (Martius a. Griess, *Zeitschr. f. Chem.* [2] i. 132; G. A. Schmidt, *ibid.* v. 417).—Produced: 1. By oxidation of aniline:

$$\underset{\text{Aniline.}}{3C^6H^7N} + O^3 = \underset{\substack{\text{Amidazo-}\\\text{benzene.}}}{C^{12}H^{11}N^3} + \underset{\text{Phenol.}}{C^6H^6O} + 2H^2O.$$

a. When nitrous acid gas is passed into a gently warmed solution of aniline in 3 pts. alcohol,* till the liquid acquires a deep red colour, and moderately strong hydrochloric acid is then added in excess, a thick brown-red pulp is produced, from which, after it has been freed by pressure from the mother-liquor and washed with weak spirit, hot water extracts hydrochloride of amidazobenzene, and from this the base may be precipitated by ammonia.—*β.* It may also be prepared by heating a mixture of 1 pt. aniline nitrate, 3 pts. sodium stannate, and 10 pts. water to 100°, gradually adding soda-ley till a sample is coloured deep-red by hydrochloric acid, then supersaturating in the cold with hydrochloric acid, digesting the separated red-brown resin with soda-ley, dissolving it in hot water containing hydrochloric acid, and precipitating with ammonia (Martius a. Griess).

2. Amidazobenzene is produced, together with amidazoxybenzene, by reduction of mononitro-azoxybenzene. The reaction appears to take place as shown by the equation:

$$3C^{12}H^9(NO^2)N^2O + 11H^2S = 2C^{12}H^9(NH^2)N^2 + C^{12}H^9(NH^2)N^2O + 8H^2O + S^{11}.$$

1 pt. of this nitro-compound is heated to boiling with 10 pts. of strong alcohol, and gradually mixed, while the boiling is continued, with a concentrated alcoholic solution of ammonium sulphide, in small portions (2–3 c.c.), each being added only after the odour of the former portion has disappeared, and the process continued till all the nitroazoxybenzene is dissolved, and a sample taken out of the liquid no longer crystallises on cooling. (If the ammonium sulphide were added more quickly, a further

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* In a cold solution the only product is diazoamidobenzene (iv. 459).

reduction would take place, resulting in the formation of aniline and paraphenylene-diamine.) The liquid decanted from the separated sulphur, freed from the greater part of the alcohol by distillation, and mixed with water, deposits a yellow lamino-crystalline mixture of amidazobenzene and amidazoxybenzene, which may be separated by the different solubilities of their hydrochlorides in dilute alcohol. The crude product drenched with weak spirit and excess of hydrochloric acid, yields a red-brown crystalline pulp, the greater part of which remains undissolved when heated to the boiling point. The whole filtered at the boiling heat yields a dark-red filtrate, which on cooling first deposits a small quantity of amidazobenzene hydrochloride in characteristic steel-blue needles; and if the solution be again filtered at the boiling heat, the filtrate yields almost pure amidazoxybenzene hydrochloride in rose-coloured laminar crystals. The united residues on the filters, repeatedly boiled with weak spirit containing hydrochloric acid, then crystallised from acidulated spirit of 50 p. c., or from very dilute aqueous hydrochloric acid, yield pure amidazobenzene hydrochloride in laminæ or needles having a dark violet-blue colour and metallic lustre. They are decomposed even by pure water, more readily by ammonia, yielding the free base (Schmidt).

3. By the action of aniline and its salts—most readily with the hydrochloride—on the isomeric compound diazo-amidobenzene, a small quantity of the aniline salt sufficing, as already explained under AROMATIC SERIES (p. 209), for the conversion of a large quantity of diazo-amidobenzene. Hence this transformation takes place to a certain extent in the preparation and in all the decompositions of diazo-amidobenzene, inasmuch as in these reactions aniline is always set free. Amidazobenzene is also found amongst the products of the action of bromine on aniline (Kekulé, *Zeitschr. f. Chem.* [2] i. 687, 689; *Jahresb.* 1866, pp. 429, 467).

Properties and Reactions.—Amidazobenzene is but very slightly soluble in water, even at the boiling heat; it dissolves more freely in ether and in hot alcohol, and crystallises from the latter in yellow rhombic needles or prisms of about 49° 20′, having their acute lateral edges perpendicularly truncated by broad faces. It melts at 130° (Martius a. Griess), at 127·4° (Schmidt),* solidifies at 120° and distils without decomposition at a temperature above the boiling point of mercury.

Amidazobenzene heated with *tin* and *hydrochloric acid* is resolved into aniline and paraphenylene-diamine:

$$C^{12}H^{11}N^3 + H^4 = C^6H^7N + C^6H^8N^2.$$

It is nearly related to diphenine or diamidazobenzene, $C^{12}H^8(NH^2)^2N^2$, and, like that compound, yields with manganese dioxide and sulphuric acid a large quantity of quinone, and with aniline-nitrate a blue colouring matter.

With *acids* amidazobenzene forms well-defined salts, most of which crystallise easily; they are decomposed by water, and their slightly acid solutions have a fine cochineal-red colour. It is a mono-acid base, its hydrochloride being $C^{12}H^{11}N^3.HCl$; the platinochloride, a red-brown crystalline precipitate, $2(C^{12}H^{11}N^3.HCl)PtCl^4$; the sulphate $(C^{12}H^{11}N^3)^2.H^2SO^4$, &c. The alcoholic solution of the base mixed with *silver nitrate* yields the compound $(C^{12}H^{11}N^3)^2.AgHO$, which crystallises in golden-yellow laminæ.

Wool and silk are coloured deep lemon-yellow by slightly acid solutions of amidazobenzene; the picrate dyes wool a fine cochineal red; but the colours are very fugitive. The oxalate of amidazobenzene constitutes aniline yellow (p. 169).

The alcoholic solution of the base kept in contact for some time, at ordinary temperatures, with ethyl iodide yields a crystalline *hydriodide of ethyl-amidazobenzene*, $C^{12}H^{10}(C^2H^5)N^3.HI$.

HYDRAZOBENZENE. $C^{12}H^{12}N^2$ (Hofmann, *Proc. Roy. Soc.* xii. 176).—This neutral body, isomeric with benzidine (which is basic), is the first product of hydrogen sulphide and other reducing agents on azobenzene, being in some cases subsequently converted into benzidine. It is prepared by passing a stream of hydrogen sulphide into a solution of azobenzene in alcoholic ammonia, whereupon the yellowish-red liquid quickly loses it colour, and on adding water hydrazobenzene is thrown down as a crystalline precipitate, which may be purified by two or three crystallisations from alcohol (Hofmann). According to Glaser, it is sometimes found amongst the products of the oxidation of aniline by potassium permanganate.

Hydrazobenzene crystallises in well-defined laminæ, slightly soluble in water, moderately soluble in alcohol and ether. It is not dissolved by acetic acid, but the stronger acids, such as hydrochloric and sulphuric, convert it into benzidine, and then dissolve it. It melts at 131° (benzidine at 118°), and is resolved by distillation into azobenzene and aniline: $2C^{12}H^{12}N^2 = C^{12}H^{10}N^2 + 2C^6H^7N$. Hydrazobenzene is also reconverted into azobenzene by oxidising agents, as nitrous acid, chlorine, bromine, iodine, potassium chromate, and potassium permanganate. The same transformation takes place when hydrazobenzene is simply moistened with alcohol, and exposed to the air. Benzidine does not undergo this change (Hofmann).

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* Schmidt found the same melting point with amidazobenzene prepared by the method of Martius a. Griess.

Azobenzene-sulphuric acid treated with hydrogen sulphide yields a sulpho-acid of hydrazobenzene (Griess).

Azoxybenzene. $C^{12}H^{10}N^2O$.—Formed by the action of sodium-amalgam, not in excess, and of ammonium sulphide, on nitrobenzene in alcoholic solution, and, together with azobenzene, by oxidation of aniline with potassium permanganate (p. 269). *Preparation* (i. 479).—By prolonged action of reducing agents it is converted into hydrazobenzene. Dichlorazoxybenzene treated in like manner is converted into dichlorhydrazobenzene (Alexejeff).

Azoxybenzene heated with strong *hydrobromic acid* to 250° in sealed tubes dissolves in it and forms dibromaniline, according to the equation

$$C^{12}H^{10}N^2O + 4HBr = 2C^6H^5Br^2N + H^2O + H^2.$$

Other products are formed at the same time, but in very small quantity, when a considerable excess of hydrobromic acid is present (Sendzink, *Zeitschr. f. Chem.* [2] vi. 266).

Amidazoxybenzene. $C^{12}H^{11}N^3O = C^{12}H^9(NH^2)N^2O$ (G. A. Schmidt, *Zeitschr. f. Chem.* [2] v. 419).—Produced, together with amidazobenzene, by the action of ammonium sulphide on nitro-azoxybenzene in alcoholic solution. The crude hydrochloride of amidazoxybenzene, crystallising, as above mentioned (p. 270), in rose-coloured laminæ, cannot be freed by recrystallisation from obstinately adhering traces of amidoazobenzene hydrochloride; but it is easily purified by dissolving it in the smallest possible quantity of hot water acidulated with hydrochloric acid, and agitating it for a few seconds with a little granulated tin till it is decolorised. The solution quickly decanted from the excess of tin (to prevent further reduction) deposits on cooling pure amidazoxybenzene hydrochloride in colourless silvery laminæ. From this salt the base may be separated by ammonia, and after one or two crystallisations from weak spirit, it is easily obtained in large tabular brittle crystals of a somewhat paler yellow colour than amidazobenzene. It is nearly insoluble in cold water, slightly soluble in boiling water, easily in strong alcohol, ether, and benzene. It melts at 138·5°, and begins to decompose at about 200°, giving off nitrogen gas, yielding a brown oily distillate containing water, aniline, and amidazobenzene, and leaving a small quantity of loose spongy charcoal. It does not appear to be converted into amidazobenzene by the action of reducing agents: ammonium sulphide does not act upon it, and by tin and hydrochloric acid it is reduced to aniline and paraphenylene-diamine.

The salts of amidazoxybenzene are colourless, well crystallised, and mostly sparingly soluble, especially the sulphate. The *hydrochloride*, $C^{12}H^{11}N^3O . HCl$, crystallises in silvery laminæ; gives off hydrochloric acid when heated, even at 100°; and, like the corresponding amidazobenzene salt, is decomposed by water, with yellow coloration. It dissolves sparingly in cold, very dilute hydrochloric acid, much more easily at the boiling heat, still more easily in acidulated alcohol. Its solution gives with *platinic chloride* a yellow indistinctly crystalline precipitate of the platino-chloride $2(C^{12}H^{11}N^3O . HCl) . PtCl^4$, slightly soluble in water and in alcohol. *Silver nitrate* added to the alcoholic solution of the base forms a precipitate consisting of long, slender, straw-yellow needles.

Trinitro-azoxybenzene. $C^{12}H^7(NO^2)^3N^2O$ (G. A. Schmidt, *Zeitschr. f. Chem.* [2] v. 421).—Produced by treating azoxybenzene with a mixture of strong nitric and sulphuric acids (with nitric acid alone only the two modifications of mononitro-azoxybenzene are formed: i. 479). 20 grms. of azoxybenzene are heated in a flask with a mixture of 200 grms. nitric acid (sp. gr. 1·50) and 100 grms. sulphuric acid (sp. gr. 1·80). It then dissolves, with considerable rise of temperature, but without emission of red fumes, and the solution, if immediately poured into water, yields a light yellow crystalline mass, caked together by a resinous substance. To remove the latter, the mass is triturated with a little water, washed on a filter, dried, and repeatedly exhausted with ether, till it no longer colours that liquid yellow (Schmidt). It is also formed by the action of strong nitric acid at the boiling heat on azobenzene, another body, probably trinitrazobenzene, being formed at the same time (Petrieff, *ibid.* vi. 264).

Trinitrazoxybenzene thus prepared is an indistinctly crystalline yellow powder, very much resembling the mononitrated compound in appearance. It is insoluble in water, dissolves very sparingly in alcohol and ether, easily in benzene, but is best crystallised from nitric acid (sp. gr. 1·38), in which it dissolves somewhat freely at the boiling heat, and separates on cooling in needle-shaped crystals recognisable by the naked eye, and looking in the mass very much like flowers of sulphur. It melts at 152°, solidifies in the crystalline form at 140°, and detonates with some violence at a stronger heat, leaving a small quantity of charcoal. When carefully heated above its melting point it does not crystallise again on cooling, but solidifies to a transparent yellow glass, which if again heated nearly to its melting point suddenly becomes crystalline: the formula of this glassy substance is $C^{12}H^7N^4O^7$.

The resinous substance dissolved by the ether, and forming about a sixth of the crude product, probably contains *dinitro-azoxybenzene*, or bodies isomeric therewith.

SULPHO DERIVATIVES OF BENZENE.

Benzene-sulphamide or **Sulphobenzolamide,** $C^6H^7NSO^2 = C^6H^5.SO^2(NH^2)$, was obtained by Stenhouse by heating ammonium benzene-sulphate to 200° (v. 489). Otto a. Ostrop (*Jahresb.* 1866, p. 570) prepare it by the action of ammonium on benzene-sulphobromide. It is also formed, together with phenyl bisulphide, by the action of hot concentrated aqueous ammonia on bromophenyloxysulphide (Otto, *Jahresb.* 1867, p. 629):

$$2C^{12}H^9BrS^2O^3 + 2NH^3 = 2C^6H^7NSO^2 + (C^6H^5)^2S^2 + Br^2.$$

It is nearly insoluble in cold, more soluble in hot ammoniacal water, dissolves easily in alcohol and ether, and crystallises in large nacreous laminæ, melting at 149°.

When 1 mol. benzene-sulphamide is heated with about 2 mol. potassium hydrate, a violent reaction takes place near the melting point of the amide, the mass becoming fluid, but soon giving off water and solidifying again. The product dissolves easily in water, and acids added to the solution throw down the unaltered amide. Probably the potassium replaces part of the typic hydrogen in the amide (with simultaneous formation of H^2O), and a compound is formed which dissolves easily in water. If the product after solidification be heated to 250°–300°, it solidifies again, and the amide is resolved into sulphurous anhydride and phenol:

$$\underset{\text{Benzene-sulphamide.}}{C^6H^5.SO^2NH^2} + 3KHO = NH^3 + \underset{\substack{\text{Potassium}\\\text{phenate.}}}{C^6H^5KO} + SO^3K^2 + H^2O$$

(Lindow a. Otto, *Zeitschr. f. Chem.* [2] iv. 39).

Chlorobenzene-sulphamide or *Sulphochlorobenzolamide*, $C^6H^6ClNSO^2$, is formed by treating chlorobenzene-sulphochloride with alcoholic ammonia, and crystallises from hot water (after the sal-ammoniac has been removed by cold water) in small needles, or by slow evaporation in large four-sided rhombic prisms. Dissolves easily in hot water, ether, and alcohol, and melts at 143°–144° (Otto a. Brummer). When heated with potassium hydrate it appears to react like benzene-sulphamide, and on adding hydrochloric acid to the solution of the product, sulphurous anhydride is evolved, and a resinous body is separated which crystallises from alcohol, but no chlorophenol appears to be formed (Lindow a. Otto).

Benzene-sulphuric or **Sulphobenzolic acid.** $C^6H^6SO^3 = C^6H^5.SO^3H$.—This acid, described in vol. v. p. 564 as *Phenyl-sulphurous acid*, is produced by oxidation of benzene-sulphurous acid, $C^6H^6SO^2$, either slowly by exposure to the air, or more quickly, together with nitrobenzene-sulphuric acid, by the action of nitric acid (Otto a. Ostrop, *Ann. Ch. Pharm.* cxli. 365). Also, together with phenyl-oxysulphide, by heating benzene-sulphurous acid with water to 130°:

$$\underset{\substack{\text{Benzene}\\\text{sulphurous acid.}}}{3C^6H^6SO^2} = \underset{\substack{\text{Benzene}\\\text{sulphuric acid.}}}{C^6H^6SO^3} + \underset{\substack{\text{Phenyl}\\\text{oxysulphide.}}}{C^{12}H^{10}S^2O^2} + H^2O$$

(Otto, *Ann. Ch. Pharm.* cxlv. 317). The sodium-salt of this acid, $C^6H^5NaSO^3$, yields by dry distillation, carbon dioxide, sulphur dioxide, and phenyl sulphide (Stenhouse, *Proc. Roy. Soc.* xiv. 351). The potassium salt heated with alkaline carbonates yields a small quantity of benzoic acid. Larger quantities of the latter are obtained by heating the benzene-sulphate with potassium cyanide, whereby phenyl-cyanide or benzonitrile, $C^6H^5.CN$, is formed, and heating the latter with potash (Merz, *Zeitschr. f. Chem.* [2] v. 33).

Benzene-sulphuric or *Sulphobenzolic chloride*, $C^6H^5SO^2Cl$, described in vol. v. p. 564 as *Phenylsulphurous chloride*, is also produced by passing chlorine into water in which benzene-sulphurous acid is suspended (Otto); 3 mol. sulphobenzol-chloride and 4 mol. potassium cyanide form a solution from which water throws down a resinous precipitate yielding to alcohol a not inconsiderable quantity of phenyl bisulphide, $(C^6H^5)^2S^2$ (Lindow a. Otto, *Zeitschr. f. Chem.* [2] iv. 40).

Chlorobenzene-sulphuric bromide, $C^6H^4ClSO^2Br$, is produced by the action of bromine on chlorobenzene-sulphurous acid (p. 275) suspended in water, and remains, on evaporating the ethereal solution, as an oil which solidifies to a crystalline mass. It melts at 52° to 53°, and is resolved by alkalis into metallic bromide and chlorobenzene-sulphite (Otto, *Jahresb.* 1867, p. 630).

Chlorobenzene-sulphuric chloride, $C^6H^4ClSO^2Cl$, is formed, together with phosphorus oxychloride, by triturating 1 mol. dry sodium sulphochlorobenzolate with 1 mol. phosphorus pentachloride, remaining undissolved when the product is treated with water. It crystallises from ether (free from alcohol) in well-defined four-sided rhombic tables, or prisms resembling those of sulphotoluol-chloride, melting at 50°–51°, insoluble in water, but easily soluble in ether and in benzene. On dissolving it in alcohol, ethylic sulphochlorobenzolate is formed, which separates as a heavy, non-distillable oil. Heated with alkalis or baryta-water, it is resolved into metallic chloride and sulphochlorobenzolate. With fuming nitric acid, after prolonged action, it forms nitrochlorobenzene-sulphuric acid (Otto a. Brummer, *Jahresb.* 1867, p. 632).

Bromobenzene-sulphuric acid, $C^6H^4Br.SO^3H$, is produced by dissolving bromobenzene in fuming sulphuric acid (Couper, *Compt. rend.* xlvi. 230). When separated from its lead-salt by hydrogen sulphide, it forms a radio-crystalline deliquescent mass, melting at 88°. It is specially distinguished by the crystallising power and beauty of its salts. The *lead salt* $(C^6H^4BrSO^3)^2Pb$ forms very characteristic, large, hemispherical aggregates, having almost the aspect of fungi; not very soluble in cold water. The *potassium salt* $C^6H^4BrSO^3K$ crystallises from water in well-developed, flat, rhombic crystals, very soluble in water. The potassium salt fused with caustic potash yields resorcin: consequently bromobenzene-sulphuric acid belongs to the para- series (1 : 4) (A. Ross Garrick, *Zeitschr. f. Chem.* [2] v. 549).

Isobromobenzene-sulphuric acid, $C^6H^4BrSO^3H$, is produced by the action of bromine on sulphobenzolic acid. The action does not take place in the cold, and is slow even at 100°; to complete it, the two substances must be heated together for several days in a sealed tube. The product is to be mixed with water, and evaporated over the water-bath till all the hydrobromic acid has evaporated, then neutralised with lead carbonate, and the resulting lead salt purified by repeated crystallisation. From this salt the acid and the other salts are prepared. All the salts of this acid are totally different from those of the preceding acid. The acid itself may be obtained in the solid state, by leaving its concentrated solution to stand for some time, but it is so deliquescent that its melting point cannot be determined. The *lead salt* $(C^6H^4BrSO^3)^2Pb + 3H^2O$ forms white granular crystals, more soluble in water than the lead salt of the preceding acid. The *potassium salt* $C^6H^4BrSO^3K + H^2O$ is extremely soluble in water, and crystallises in small stellate groups. The salt fused with potassium-hydrate appears to yield hydroquinone, showing that the acid belongs to the ortho- series (1 : 2). Hence it appears that the group SO^2HO introduces the bromine into the same place as the group COHO in benzoic acid (Ross Garrick, *loc. cit.*). According to R. Genz (*ibid.* 692), the acid prepared by the action of bromine on sulphobenzolic acid appears to yield resorcin as well as hydroquinone when fused with potash.

Chlorobenzene-sulphuric or *Sulphochlorobenzolic acid*, $C^6H^4Cl.SO^3H$, is produced by heating monochlorobenzene with fuming sulphuric acid. When separated from its lead-salt by hydrogen sulphide and evaporated, it remains as a syrup, which when left over oil of vitriol crystallises in large deliquescent prisms. Its salts are very stable. The sodium salt $C^6H^4ClSO^3Na.H^2O$ forms cubic crystals; the *silver salt* $C^6H^4ClSO^3Ag$, nacreous scales; the *barium salt* $(C^6H^4ClSO^3)^2Ba.2H^2O$, also nacreous scales; the *lead salt* $(C^6H^4ClSO^3)^2Pb.5H^2O$, a laminar mass; the *copper salt* $(C^6H^4ClSO^3)^2Cu.5H^2O$, greenish needles (Glutz, *Ann. Ch. Pharm.* cxliii. 181; Otto a. Brummer, *ibid.* 100).

Sodium-amalgam converts the acid into benzene-sulphuric acid, identical with that formed from benzene and sulphuric acid. The chlorinated acid is not acted upon by zinc and sulphuric acid, or by boiling potash-ley. In concentrated solution it is oxidised by a mixture of potassium chromate and sulphuric acid, with evolution of chlorine and carbon dioxide. The lead salt yields with nitric acid, nitrochlorobenzene-sulphate and sulphate of lead, together with nitrochlorobenzene, $C^6H^4Cl(NO^2)$, which melts at 75° and solidifies at 65°–60° (Glutz). The sodium salt triturated with phosphorus pentachloride yields chlorobenzene sulphochloride, $C^6H^4ClSO^2Cl$, together with phosphorus oxychloride (Otto a. Brummer). The potassium salt fused with a small quantity of potash turns red and probably forms chlorophenol; heated with twice its weight of potassium hydrate, till the red colour almost disappears, it yields resorcin: consequently the acid belongs to the para- series (Oppenheim a. Vogt, *Zeitschr. f. Chem.* [2] v. 722).

Dichlorobenzene-sulphuric or *Sulphodichlorobenzolic Acid.* $C^6H^3Cl^2.SO^3H$ (Lesimple, *Zeitschr. f. Chem.* [2] iv. 226).—Fuming sulphuric acid does not act on dichlorobenzene at ordinary temperatures, and may therefore be used for the separation of mono- and di-chlorobenzene. But when the latter is strongly heated and occasionally agitated with excess of the fuming acid, it dissolves completely, and the sulpho-acid crystallises out on cooling. An easier method of preparing it is to pass the vapour of sulphuric anhydride into a flask containing dichlorobenzene, dissolve the product in water, and treat the filtered solution as above. The acid, separated from the purified lead-salt by hydrogen sulphide, crystallises from aqueous solution in small colourless rhombic prisms, containing 2 at. water, melting at a temperature above 100°, easily soluble in water, sparingly in ethereal liquids. Its salts crystallise with great facility, dissolve somewhat sparingly in water, are nearly insoluble in alcohol and ether, and bear a temperature of more than 200° without decomposition, but decompose at a red heat, with evolution of sulphurous anhydride:

Potassium salt,	$C^6H^3Cl^2SO^3K.H^2O$,	small prisms and tables.
Sodium ,,	$C^6H^3Cl^2SO^3Na.H^2O$,	six-sided tables.
Ammonium ,,	$C^6H^3Cl^2SO^3(NH^4).H^2O$,	needles moderately soluble in water.
Silver ,,	$C^6H^3Cl^2SO^3Ag$,	greyish-white nacreous pointed needles.
Barium ,,	$(C^6H^3Cl^2SO^3)^2Ba$,	laminæ.
Magnesium ,,	$(C^6H^3Cl^2SO^3)^2Mg.6H^2O$,	colourless interlaced needles.
Lead ,,	$(C^6H^3Cl^2SO^3)^2Pb.3H^2O$,	tufts of needles, or large crystals which on exposure to air give off water and assume a dull appearance like porcelain.

3. *Benzene-disulphuric* or *Disulphobenzolic acid*, $C^6H^4\begin{cases}SO^2HO\\SO^2HO\end{cases}$, discovered by Buckton and Hofmann, is prepared by heating sulphobenzolic acid for two hours with an equal volume of fuming sulphuric acid. The *lead salt* $C^6H^4(SO^3)^2Pb + 2H^2O$ forms small granular crystals, very soluble in water. The *potassium salt* $C^6H^4(SO^3K)^2 + 1\frac{1}{2}H^2O$ crystallises in small, but well-defined, shining, transparent crystals, easily soluble in water. Heated to 230° with excess of potassium hydrate, it yields resorcin; consequently, disulphobenzolic acid, like sulphobromobenzolic acid, belongs to the para- series (1 : 4). Its potassium salt, distilled with potassium cyanide, yields dicyanobenzene, $C^6H^4(CN)^2$ (Ross Garrick, *loc. cit.*).

Benzene-sulphurous Acid. $C^6H^5.SO^2H$ (Otto a. Ostrop, *Ann. Ch. Pharm.* cxli. 365; Otto, *ibid.* cxlv. 317).—This compound, discovered by Kolbe, and described in vol. v. p. 564 as *Phenylsulphurous hydride*, was originally obtained as a zinc-salt by the action of zinc-ethyl on benzene-sulphochloride (phenylsulphurous chloride). Otto and Ostrop find that it may be more easily prepared by treating this chloride with sodium-amalgam:

$$C^6H^5SO^2Cl + Na^2 = NaCl + C^6H^5SO^2Na.$$

Perfectly dry benzene-sulphochloride (50–60 grms.) is mixed with several times its volume of pure anhydrous ether in a retort provided with an upright condenser, and sodium-amalgam is added by small portions, till a sample, freed from ether by evaporation, no longer smells of benzene-sulphochloride, and forms a clear solution in water. When the reaction is completed, the ether is evaporated off on the water-bath; the sodium salt is dissolved in the smallest possible quantity of water; the clear decanted solution is mixed with hydrochloric acid; and the separated acid, $C^6H^6SO^2$, is freed from an adhering oily body by crystallisation from hot deaërated water, as far as possible apart from the air.

Benzene-sulphurous acid thus obtained crystallises in stellate groups of large prisms, exhibiting the properties described by Kolbe (i. 565). Its aqueous solution first reddens litmus and then bleaches it. The crystals melt at 68°–69°, and decompose when heated above 100°. They deliquesce in the air, taking up oxygen and forming benzene-sulphuric acid, $2C^6H^6SO^3.3H^2O$.

Benzene-sulphurous acid dissolves in moderately concentrated nitric acid, forming benzene-sulphuric and nitrobenzene-sulphuric acids. Fuming nitric acid attacks it strongly, forming a nitro-compound, $C^{16}H^{18}N^2S^3O^6$, which is precipitated by water, and crystallises from alcohol in hard vitreous rhombohedral crystals, having two of their diametrically opposite lateral edges truncated; it melts at 98·5°, detonates slightly on platinum foil, is insoluble in water and ether, but easily soluble in alcohol; its constitution has not been exactly determined. The aqueous solution filtered from this compound contains nitrobenzene-sulphuric acid (Otto a. Ostrop).

Benzene-sulphurous acid heated with water to 130° is resolved (analogously to toluene-sulphurous acid, p. 288) into phenyl oxysulphide and benzene-sulphuric acid:

$$3C^6H^6SO^2 = C^{12}H^{10}S^2O^2 + C^6H^6SO^3 + H^2O.$$

Its *potassium salt*, heated to 250°–300° with rather more than 1 mol. potassium hydrate, yields benzene and potassium sulphite:

$$C^6H^5SO^2K + KHO = C^6H^6 + SO^3K^2.$$

The acid suspended in water into which a stream of chlorine gas is passed is converted into benzene-sulphochloride (Otto); by bromine, in like manner, into benzene-sulphobromide (Otto a. Ostrop).

Chlorobenzene-sulphurous Acid. $C^6H^4Cl.SO^2H$ (Otto a. Brummer, *Ann. Ch. Pharm.* cxliii. 191).—Produced by the action of sodium-amalgam on chlorobenzene-sulphochloride. When separated from the resulting sodium salt and recrystallised from water, with addition of animal charcoal, it forms long four-sided rhombic prisms, which melt at 88°–90°, dissolve sparingly in cold, easily in hot water, also in alcohol and ether:

Sodium salt, $C^6H^4ClSO^2Na.2H^2O$, four-sided rhombic tables.
Barium „ $(C^6H^4ClSO^2)^2Ba$ }, small needles.
Calcium „ $(C^6H^4ClSO^2)^2Ca$ }
Lead „ $(C^6H^4ClSO^2)^2Pb$, crystalline precipitate.

Ethyl Chlorobenzene-sulphite, $C^6H^4ClSO^2(C^2H^5)$, produced by heating the acid with alcohol containing hydrochloric acid, is precipitated by water, as an oil which solidifies in the crystalline form, and crystallises from alcohol in small needles melting at 123°. Converted by aqueous chromic acid into chlorobenzene-sulphuric acid, by chlorine-water into chlorobenzene-sulphochloride, and by zinc and sulphuric acid into chlorophenylic sulphydrate.

Sulphobenzide. $C^{12}H^{10}SO^2$.—Discovered by Mitscherlich, who obtained it by the action of sulphuric anhydride on benzene (v. 486). It is also produced by treating benzene with sulphuric chlorhydrate: $SO^2(HO)Cl + 2C^6H^6 = C^{12}H^{10}SO^2 + H^2O + HCl$ (Karl Knapp, *Zeitschr. f. Chem.* [2] v. 41). Stenhouse's sulphobenzolene (v. 489), obtained by oxidation of phenyl sulphide, $C^{12}H^{10}S$, and originally regarded as isomeric with sulphobenzide, is really identical therewith, the melting point of sulphobenzide being, according to Knapp, 125°–126°, which is the same as that of sulphobenzolene. (See also Kekulé a. Szuch, *Bull. Soc. Chim.* [2] viii. 204.)

Sulphobenzide dissolves without alteration in hot dilute sulphuric acid, and crystallises out again on cooling; but the concentrated acid dissolves it with blackening and formation of sulphobenzolic acid: $C^{12}H^{10}SO^2 + SO^4H^2 = 2C^6H^6SO^3$. It is not acted upon by alcoholic potash, even at 180° in sealed tubes (Gericke, *Ann. Ch. Pharm.* c. 207).

The results of the action of chlorine on sulphobenzide have been variously stated by different chemists. According to Gericke, an additive compound, $C^{12}H^{10}SO^2.Cl^4$, or $\left.\begin{matrix}Cl^2.C^6H^5SO^2\\Cl^2.C^6H^5\end{matrix}\right\}$, is formed, either at ordinary temperatures in diffused daylight, or more quickly in direct sunshine, or when the sulphobenzide is heated to its melting point; and this compound is resolved by rapid heating, or by the action of potash, into hydrochloric acid and dichlorosulphobenzide: $C^{12}H^{10}SO^2Cl^4 = 2HCl + C^{12}H^8Cl^2SO^2$. According to Otto a. Ostrop, on the contrary (*Ann. Ch. Pharm.* cxli. 93), chlorine, either dry or moist, exerts no action whatever on sulphobenzide in diffused daylight at ordinary temperatures; but if the sulphobenzide be heated to its melting point, it is resolved by chlorine in diffused daylight into monochlorobenzene and benzene-sulphochloride:

$$C^{12}H^{10}SO^2 + Cl^2 = C^6H^5Cl + C^6H^5ClSO^2.$$

In direct sunshine, according to the same chemists, chlorine acts on sulphobenzide at ordinary temperatures, producing an oily mixture of several chlorinated benzenes, and a crystalline body consisting of monochlorobenzene hexchloride, $C^6H^5Cl.Cl^6$ (see p. 264). These results have been fully confirmed by the more recent experiments of Otto a. Gruber (*Zeitschr. f. Chem.* [2] iv. 630). Sulphobenzide dissolved in carbon bisulphide, either pure or containing iodine, is not attacked by chlorine either in shade or in sunshine, the action of the chlorine being entirely confined to the solvent.

Neither does sulphobenzide take up chlorine when suspended in water containing iodine, and treated therewith (Otto a. Gruber).

A modification of sulphobenzide called by Stenhouse *parasulphobenzide* * is obtained by oxidation of parasulphide of phenyl. It melts at 230°, is soluble in boiling alcohol, from which it crystallises in long white shining needles; insoluble in water, soluble in benzol, ether, and carbon bisulphide; dissolves readily without blackening in warm sulphuric acid, and is precipitated unchanged by water. It dissolves also in hot strong nitric acid and crystallises out on cooling (*Proc. Roy. Soc.* xviii. 543).

Dichlorosulphobenzide, $C^{12}H^8Cl^2SO^2$, is produced by exposing sulphobenzide, mixed with a few grains of iodine and heated to 100°, to a slow stream of dry chlorine in diffused daylight, till it is wholly converted into a viscid non-crystallising mass. The remainder of the iodine is then expelled by chlorine; the product is washed with warm water containing a little sodium carbonate, then dissolved in ether; and the ethereal solution is evaporated. Dichlorosulphobenzide thus obtained is a thickish, transparent, nearly colourless oil, which becomes mobile when warmed; heavier than water, insoluble therein, easily soluble in ether and in benzol, less soluble in absolute alcohol. It has a faint odour, becoming stronger on warming, and distantly resembling those of chlorobenzol and camphor; distils without decomposition at a temperature above 300°. It is not altered by alcoholic potash or by sodium-amalgam, if the latter be kept in contact with its solution in anhydrous benzene; but in alcoholic solution it is quickly decomposed by sodium-amalgam, yielding products not yet examined (Otto a. Gruber).

A compound isomeric with this liquid dichlorosulphobenzide, and crystallising in beautiful silky inodorous needles melting at 140°–141°, is obtained by the action of sulphuric anhydride on monochlorobenzene (Otto, p. 265).

Representing sulphobenzide by the formula

$$\left.\begin{matrix}C^6H^5SO^2\\ C^6H^5\end{matrix}\right\}\quad\text{or}\quad C^6H^5—S—O—O—C^6H^5,$$

the crystalline modification of dichlorosulphobenzide may perhaps be represented as $\left.\begin{matrix}C^6H^4ClSO^2\\ C^6H^4Cl\end{matrix}\right\}$ or $C^6H^4Cl—S—O—O—C^6H^4Cl$, and the liquid modification produced by the action of chlorine in presence of iodine on sulphobenzide, as $\left.\begin{matrix}C^6H^3Cl^2SO^2\\ C^6H^5\end{matrix}\right\}$ $= C^6H^3Cl^2—S—O—O—C^6H^5$, or as $\left.\begin{matrix}C^6H^5SO^2\\ C^6H^3Cl^2\end{matrix}\right\} = C^6H^5—S—O—O—C^6H^3Cl^2$. The reaction of sulphobenzide with chlorine in diffused daylight, at its melting point, whereby it is resolved into monochlorobenzene and sulphobenzolic chloride, justifies the formula assigned to it by Kekulé, viz. $C^6H^5—S—O—O—C^6H^5$: for if the *two* benzene-residues were symmetrically united with the oxygen, as represented by the formula $C^6H^5—O—S—O—C^6H^5$, the action of chlorine should give rise to sulphuryl chloride and chlorinated derivatives of benzene (Otto a. Gruber, *Ann. Ch. Pharm.* cxlix. 174).

Nitrosulphobenzide, $C^{12}H^9(NO^2)SO^2$, is produced by heating sulphobenzide with fuming nitric acid till it is completely dissolved. On adding water, and treating the resulting precipitate with hot alcohol, nitrosulphobenzide dissolves, while dinitrosulphobenzide remains behind; and the hot saturated solution deposits nitrosulphobenzide on cooling, as a honey-yellow unctuous mass which solidifies on cooling. It melts at 90°–92°, decomposes completely at 250°, is but slightly soluble in water either hot or cold, easily soluble in ether. From solution in dilute alcohol, it separates on cooling in soft microscopic crystals. *Dinitrosulphobenzide*, $C^{12}H^8(NO^2)^2SO^2$, is obtained by prolonged boiling of sulphobenzide with fuming nitric acid, or more quickly by the action of a mixture of fuming nitric and sulphuric acids. It forms small white silky rhombic tables, insoluble in water, slightly soluble in alcohol and ether; melts at 164°; solidifies in a radio-crystalline mass; and sublimes without decomposition below 320° (Gericke, *loc. cit.*).

Amidosulphobenzide, $C^{12}H^9(NH^2)SO^2$, is produced by the action of ammonium sulphide on nitrosulphobenzide dissolved in alcohol. When purified by solution in hydrochloric acid and precipitation by potash, it forms microscopic prisms, slightly soluble in cold water, easily in hot water and in alcohol. The *hydrochloride*, $C^{12}H^9(NH^2)SO^2.HCl$, crystallises in reddish four-sided prisms, easily soluble in water and in alcohol, melting at about 90°. The *platinochloride*, $2[C^{12}H^{8}(NH^2)SO^2.HCl].PtCl^4$, is a yellowish-brown amorphous precipitate soluble in alcohol.

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* As the prefix 'para,' when applied to aromatic bodies, has a peculiar signification not here implied, it would perhaps be better to call this modification *isosulphobenzide*.

Diamidosulphobenzide, $C^{12}H^{8}(NH^2)^2SO^2$, is obtained by the action of ammonium sulphide on dinitrosulphobenzide, and is thrown down from its solution in hydrochloric acid by potash, as a yellowish-white precipitate, which soon becomes darker. It dissolves with difficulty in cold, easily in hot water and alcohol, and crystallises in four-sided prisms, easily melting to a brown mass. The *hydrochloride*, $C^{12}H^{8}(NH^2)^2SO^2.2HCl$, crystallises in long reddish rhombic prisms, easily soluble in water and in alcohol, not decomposing at 100°. Its solution forms with *platinic chloride* a brown-red indistinctly crystalline precipitate, consisting of $2[C^{12}H^{8}(NH^2)SO^2.2HCl].PtCl^4$ (Gericke).

BENZENE, HOMOLOGUES OF. C^nH^{2n-6}.—The derivation of these hydrocarbons from benzene, the general methods of producing them synthetically, and the nature of the isomerism existing in the several groups of hydrocarbons and their derivatives, have been discussed in the article AROMATIC SERIES. Those which occur in coal-tar naphtha (C^7H^8, C^8H^{12}, C^9H^{12}) appear to be methylic derivatives, coal-tar cumene, for example, being trimethyl-benzene, $C^6H^3(CH^3)^3$. Toluene and xylene have been found, together with benzene, among the hydrocarbons produced by subjecting to dry distillation the lime-soap of Menhaden oil (Warren a. Storer, *Zeitschr. f. Chem.* iv. 229).

The specific gravities and expansions of these hydrocarbons have been determined by Louguinine (*Ann. Ch. Phys.* [4] xi. 153; also with remarks by H. Kopp, *Ann. Ch. Pharm. Suppl.* v. 295, 303; *Zeitschr. f. Chem.* [2] iv. 194). The specific gravities at 0° were found to be as follows:

	Sp. gr. at 0°
Benzene, from benzoic acid	0·8995
Toluene, from coal-tar: B. P. 111°–111·5°	0·8841
Xylene, from coal-tar: B. P. 138°–139°	0·8770
Cymene, from Roman cumin-oil: B. P. 175°–176° . .	0·8703
Cymene, from camphor:* B. P. 174°–175°	0·8732

Hence it appears that: 1. The densities at 0° of the aromatic hydrocarbons decrease as they ascend in the series from benzene to cymene.—2. The successive differences exhibit a certain regularity, that between benzene and toluene being 0·0154, and that between toluene and xylene 0·0071, or nearly half the preceding. Calling the first difference a, the second will be $\frac{a}{2}$; and if we suppose the same law to hold good throughout the series, the difference of density between xylene and cumene will be $\frac{a}{4}$, and that between cumene and cymene $\frac{a}{8}$. Accordingly the density of cymene should be equal to that of benzene diminished by

$$a + \frac{a}{2} + \frac{a}{4} + \frac{a}{8};$$

that is, by $0{\cdot}0154 + 0{\cdot}0077 + 0{\cdot}0039 + 0{\cdot}0019 = 0{\cdot}0289$; this would give for the density of cymene

$$d = 0{\cdot}8995 - 0{\cdot}0289 = 0{\cdot}8706,$$

which is nearly the same as the experimental number 0·8075.

The specific volumes of the five hydrocarbons, that of each at 0° = 1, are calculated by means of the following interpolation formulæ:

$v = 1{\cdot}0000 + 0{\cdot}00116t + 0{\cdot}000002226t^2$ for Benzene.
$v = 1{\cdot}0000 + 0{\cdot}001028t + 0{\cdot}000001779t^2$ „ Toluene.
$v = 1{\cdot}0000 + 0{\cdot}0009506t + 0{\cdot}000001632t^2$ „ Xylene.
$v = 1{\cdot}0000 + 0{\cdot}0008952t + 0{\cdot}000001277t^2$ „ Cymene from Cumin-oil.
$v = 1{\cdot}0000 + 0{\cdot}000898t + 0{\cdot}000001311t^2$ „ Cymene from Camphor.

The following table contains the volumes of these five hydrocarbons at different temperatures: I. As calculated from the preceding interpolation formulæ; II. As deduced from the expansion curve constructed according to Louguinine's experiments:

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[*] Cymene from camphor is in all probability identical with that from Roman cumin-oil. Kopp doubts the purity of the hydrocarbons used in Louguinine's experiments, inasmuch as none of them, except the benzene, exhibited constant boiling points.

	Benzene		Toluene		Xylene		Cymene from Rom. Cumin-oil		Cymene from Camphor	
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
0°	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
10	1·0118	1·0122	1·0104	1·0104	1·0096	1·0094	1·0090	1·0093	1·0090	1·0092
20	1·0241	1·0245	1·0213	1·0214	1·0197	1·0195	1·0184	1·0190	1·0184	1·0186
30	1·0368	1·0371	1·0324	1·0324	1·0300	1·0297	1·0280	1·0285	1·0282	1·0282
40	1·0500	1·0500	1·0439	1·0438	1·0407	1·0403	1·0378	1·0379	1·0380	1·0378
50	1·0636	1·0622	1·0558	1·0554	1·0516	1·0513	1·0480	1·0478	1·0481	1·0478
60	1·0776	1·0774	1·0681	1·0678	1·0629	1·0626	1·0583	1·0583	1·0586	1·0584
70	1·0921	1·0919	1·0807	1·0804	1·0745	1·0739	1·0692	1·0690	1·0693	1·0689
80	1·1070	1·1065	1·0937	1·0937	1·0865	1·0859	1·0798	1·0800	1·0802	1·0799
90			1·1069	1·1069	1·0987	1·0985	1·0910	1·0912	1·0914	1·0913
100			1·1206	1·1206	1·1113	1·1113	1·1023	1·1026	1·1029	1·1056 ?

By extending the interpolation formulæ above given to temperatures beyond the limits of Louguinine's experiments (which process of *extra-polation* has been found in other cases to give results agreeing with those of observation), Kopp has calculated the specific volumes of the five hydrocarbons at the boiling points given by Louguinine, that of each hydrocarbon at 0° being taken as unity: for benzene and cymene the numbers deduced from Kopp's own experiments are also given:

$$
\begin{array}{llll}
\multicolumn{4}{c}{\textit{According to Louguinine.}} \\
 & & \text{Sp. vol.} & \text{Diff.} \\
C^6H^6 & \text{for } 81^\circ & 96{\cdot}1 & \left.\begin{matrix} \\ \\ \end{matrix}\right\} 22{\cdot}1 \\
C^7H^8 & ,,\ 111^\circ & 118{\cdot}2 & \left.\begin{matrix} \\ \\ \end{matrix}\right\} 22{\cdot}3 \\
C^8H^{10} & ,,\ 138^\circ & 140{\cdot}5 & \left.\begin{matrix} \\ \\ \end{matrix}\right\} 2 \times 21{\cdot}8 \\
C^{10}H^{14*} & ,,\ 175^\circ & 184{\cdot}1 &
\end{array}
\qquad
\begin{array}{llll}
\multicolumn{4}{c}{\textit{According to Kopp.}} \\
 & & \text{Sp. vol.} & \text{Diff.} \\
C^6H^6 & \text{for } 81^\circ & 96{\cdot}1 & \left.\begin{matrix} \\ \\ \\ \\ \\ \end{matrix}\right\} 4 \times 21{\cdot}9 \\
C^{10}H^{14*} & ,,\ 175^\circ & 183{\cdot}5 &
\end{array}
$$

Hence it appears that in this series of liquid hydrocarbons, the specific volumes at the boiling points differ by about *n* × 22 for a difference in the formulæ of *n* CH^2.

Hydrocarbon C^7H^8.

The only hydrocarbon of the series containing 7 at. carbon is **methyl-benzene** or **toluene**, $C^6H^5(CH^3)$. To the modes of formation of this body already mentioned (v. 851) must be added: *α*. The passing of the vapour of ethyl-benzene through a red-hot tube, naphthalene, $C^{10}H^8$, and its hydride, $C^{10}H^{10}$, being formed at the same time (Berthelot, *Zeitschr. f. Chem.* [2] iv. 589):

$$3C^6H^5(C^2H^5) = 2C^7H^8 + C^{10}H^8 + 3H^2$$

and

$$3C^6H^5(C^2H^5) = 2C^7H^8 + C^{10}H^{10} + 2H^2.$$

β. The heating of nitric acid with lime (Baeyer, *ibid.* 119).—*γ*. The dry distillation of the lime-salt of Menhaden oil (p. 278).

Toluene, agitated with an alkaline solution of *potassium permanganate*, yields benzoic acid, and a neutral solid aromatic body, insoluble in water and in alkalis, soluble in ether, but no phthalic acid (Berthelot, *Bull. Soc. Chim.* [2] vii. 124). Heated with 80 pts. of strong *hydriodic acid*, it is completely converted into septane, C^7H^{16}; with 20 pts. of the acid it yields propane and charcoal:

$$C^7H^8 + 2HI = C^3H^8 + C^4 + H^2 + I^2$$

(Berthelot, *ibid.* 53). Treated with *hydriodide of phosphine*, $PH^3.HI$, it takes up 2 at. H, and is converted into methyl-benzolone, C^7H^{10} (Baeyer, *Zeitschr. f. Chem.* [2] iv. 445). Toluene introduced into the stomach is converted into hippuric acid, which is found in the urine (Schultzen a. Naunyn, *ibid.* 29).

Bromotoluenes. *Monobromotoluene*, $C^6H^4Br.CH^3$, boils, according to Kekulé (*Ann. Ch. Pharm.* cxxxvii. 198), at 182·5°–183° (corr. 185°–185·5°), and has a sp. gr. of 1·4109 at 22° (referred to water at 0°). *Benzyl bromide*, $C^6H^5.CH^2Br$, boils at 197°–199·5° (corr. 201·5°–202·5°), and has a sp. gr. of 1·4380 at 22°.

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* From Roman cumin-oil.

According to Beilstein (*Ann. Ch. Pharm.* cxliii. 369), the action of bromine on boiling toluene always produces benzyl bromide more or less mixed with bromotoluene; but when toluene is acted upon by bromine in presence of iodine, the only product formed, even at the boiling heat, is bromotoluene, which may thus be easily obtained pure. Cannizzaro finds (*Ann. Ch. Pharm.* cxli. 198) that the product formed by the action of bromine on toluene at comparatively low temperatures consists of a mixture of bromotoluene and benzyl bromide. When toluene, boiling between 110° and 114°, is mixed by drops with bromine in a well-cooled vessel, and the brominated product, after washing with water and sodium carbonate, and drying with calcium chloride, is distilled, the liquid which passes over between 160° and 190° consists mainly of bromotoluene, and that which distils at 190°–200° of benzyl bromide. On these observations Fittig (*Ann. Ch. Pharm.* cxlvii. 39) founds a process for obtaining pure bromotoluene free from benzyl bromide. Pure toluene contained in a retort standing in cold water is mixed gradually, and by very small portions, with somewhat less than the theoretical quantity of bromine, made to flow into it through a funnel-tube; and the mixture, after standing for 12 hours, is washed with soda-ley and water, dried over calcium-chloride, and distilled, the portion which goes over between 178° and 181° being collected apart. The bromotoluene thus obtained is freed from hydrobromic acid, by blowing a stream of air over it while it is briskly agitated; and by a second distillation, a colourless liquid is obtained which boils between 179° and 180°, gives off vapours which do not at all irritate the eyes, and solidifies completely in a freezing mixture.

Monobromotoluene exhibits two modifications besides the metameric compound benzyl bromide, $C^6H^4.CH^2Br$, viz. *orthobromotoluene* (1,2), which is fluid at ordinary temperatures, and *parabromotoluene* (1,4), which is crystalline. Ordinary liquid bromotoluene, obtained by the processes above described, consists mainly of the solid modification held in solution by a small quantity of the liquid. It may be made to solidify by treating it with fuming sulphuric acid; the portion not attacked by the acid then solidifies on slight cooling, in crystals, which melt at 28°–29°. Again, if ordinary bromotoluene be freed from benzyl bromide by treatment with alcoholic ammonium sulphide and subsequent distillation, the portions distilling at 178°–179°, 181°, and 182° being perfectly dried and then cooled, and the crystals which separate be taken out of the still liquid portion and dried on bibulous paper, they will then no longer melt at the ordinary temperature of a room, but only at 28°–29° (Hübner a. Wallach, *Zeitschr. f. Chem.* [2] v. 22, 138, 499).

Parabromotoluene forms shining, rather hard crystals, belonging to the rhombic system, melting at 28·5°, and boiling at 181°–183°. By oxidation with chromic acid it is converted into *parabromobenzoic acid*, melting at a temperature above 230°. By converting it into nitrobromotoluene, reducing this compound to bromotoluidine with tin and hydrochloric acid, and treating this base with sodium-amalgam, toluidine is obtained, boiling at 196° and remaining fluid at −21° (identical with Rosenstiehl's pseudo-toluidine).

The liquid bromotoluene, separated from the crystallised modification by pressure between cooled metallic plates, likewise boils at 181°–183°, but deposits only a few crystals at −20° (Rosenstiehl a. Nikiforoff, *Zeitschr.* [2] v. 635). Wroblevsky (*ibid.* 322) obtains this same modification of bromotoluene by converting nitrate of bromotoluidine, by Griess's process, into the corresponding diazo-compound (v. 867), and decomposing the sulphate of this base with absolute alcohol. The bromotoluene thus obtained is a colourless liquid, having a faint odour and boiling at 182°. By oxidation with chromic acid it is converted into *orthobromobenzoic acid*, melting at 153°, and identical with that which is obtained from ordinary benzoic acid: hence the liquid bromotoluene is orthobromotoluene (1,2).

A mixture of ethyl chlorocarbonate and sodium-amalgam acts upon bromotoluene in the same manner as on bromobenzene (p. 263), forming ethyl toluate, $C^8H^7(C^2H^5)O^2$. Benzyl-bromide treated in like manner yields the ethylic ether of an aromatic acid, $C^{15}H^{14}O^2$, which appears to be formed by the union of two benzyl groups (Wurtz, *Zeitschr. f. Chem.* [2] v. 385).

Dibromotoluene, $C^7H^6Br^2 = C^6H^3Br^2.CH^3$, is formed by the action of bromine in excess on toluene at ordinary temperatures—but only in small quantity, even after a considerable time—and separates in crystals from the portion of the product of higher boiling point. It crystallises from alcohol in long colourless needles, melting at 107°–108°; boils without decomposition at about 245°; and dissolves easily in hot, less easily in cold alcohol. It is not attacked by alcoholic potash, or by a mixture of potassium dichromate and sulphuric acid (Fittig).

Another modification of dibromotoluene is obtained by direct bromination of orthobromotoluene. It remains liquid at −20°, boils without decomposition at 236°, has a sp. gr. of 1·8127 at 19°, dissolves easily in alcohol, is not oxidised by chromic acid (Wroblevsky, *Zeitschr. f. Chem.* [2] vi. 289).

Benzylene Bromide, $C^6H^5.CHBr^2$, metameric with the preceding, is obtained by gradually adding phosphorus pentabromide to benzoic aldehyde, $C^6H^5.CHO$, and digesting the product for a few hours in the water-bath with excess of the pentabromide; purified by washing with aqueous potash and with a strong solution of sodium bisulphite, then drying, and distilling in a vacuum. It is a strongly refracting liquid, which becomes red on exposure to light; very soluble in alcohol and ether, insoluble in water. Decomposed by distillation under ordinary pressure, but distils between 130° and 140° under a pressure of 20 mm. Decomposed by sodium at about 180°, yielding toluene and a black resinous residue, which when distilled in a current of steam, solidifies to a crystalline mass of benzyl, $C^{14}H^{14}$ (Michaelson a. Lippmann, *Bull. Soc. Chim.* [2] iv. 251).

Chlorotoluenes. *Orthomonochlorotoluene*, $C^6H^4Cl.CH^3$, is obtained from chlorinated orthotoluidine (see TOLUIDINES) by converting the latter, by Griess's process, first into nitrate, then into sulphate of diazochlorotoluene, and boiling this sulphate with alcohol. It is a colourless liquid, which boils at 156° and is converted by oxidation into orthochlorobenzoic acid (Wroblewsky, *Zeitschr. f. Chem.* [2] v. 460). *Paramonochlorotoluene*, $C^6H^2ClH^2.CH^3$, and the metameric body *Benzyl chloride*, $C^6H^5.CH^2Cl$, are described in vol. v. pp. 853, 854.

Of the three *dichlorinated toluenes*, $C^7H^6Cl^2$,

$C^6H^3Cl^2.CH^3$	$C^6H^4Cl.CH^2Cl$	$C^6H^5.CHCl^2$
Dichlorotoluene	Chlorobenzyl chloride	Benzylene chloride,

the second and third are also described in vol. v. pp. 854, 855. The following additional observations are by Beilstein a. Geitner (*Jahresb.* 1866, p. 590) and Neuhof (*Zeitschr. f. Chem.* [2] ii. 653; *Jahresb.* 1866, p. 597).

1. *Dichlorotoluene*, $C^6H^3Cl^2.CH^3$, is obtained (together with monochlorotoluene) by passing chlorine into toluene mixed with iodine. It is liquid, boils at 196° (Beilstein a. Geitner), 197°–199° (Neuhof), and retains its two chlorine-atoms with equal force. By oxidation with chromic acid, it is converted into *paradichlorobenzoic* (dichlorodracylic) acid:

$$C^6H^3Cl^2.CH^3 + O^3 = H^2O + C^6H^3Cl^2.CO^2H.$$

2. *Chlorobenzyl chloride*, $C^6H^4Cl.CH^2Cl$, is produced by the action of chlorine on monochlorotoluene at the boiling heat, or by the action of chlorine in the cold, in presence of iodine, on benzyl chloride. It boils at 212°–214°, gives up *one* of its chlorine-atoms more easily than the other, and is accordingly converted by oxidation into *paramonochlorobenzoic* (chlorodracylic) acid (Neuhof):

$$C^6H^4Cl.CH^2Cl + O^2 = HCl + C^6H^4Cl.CO^2H.$$

By boiling with alcoholic solution of potassium sulphydrate, it is converted into an oily mercaptan which crystallises from alcohol:

$$C^6H^4Cl.CH^2Cl + KHS = KCl + C^6H^4Cl.CH^2SH.$$

Boiled with alcoholic potassium cyanide, it yields the amide of alpha-toluic acid:

$$C^6H^4Cl.CH^2Cl + KCN + H^2O = KCl + C^7H^6Cl.COH^2N.$$

Heated with the solution of potassium cyanide in a sealed tube, it yields the nitrile of alpha-toluic acid (Neuhof).

3. *Benzylene chloride*, *Chlorobenzol*, or *Bitter almond oil chloride*, $C^6H^5.CHCl^2$, is produced by passing chlorine into benzyl chloride at the boiling heat, or (i. 855) by the action of phosphorus pentachloride on bitter almond oil.

Of the *trichlorinated compound* $C^7H^5Cl^3$, there are four possible modifications, depending on the distribution of the chlorine-atoms between the principal and lateral chains: viz.,

Trichlorotoluene,	$C^6H^2Cl^3.CH^3$	boiling at	235°.
Benzotrichloride,	$C^6H^5.CCl^3$,	„	214°.
Dichlorobenzyl-chloride,	$C^6H^3Cl^2.CH^2Cl$,	„	241°.
Chlorbenzylene-chloride,	$C^6H^4Cl.CHCl^2$,	„	234°.

The first and third may also admit of further modifications depending on the relative positions of the chlorine-atoms in the principal chain.

The second and third of the above compounds are described in vol. v. p. 855.

They have been further studied, together with the other two, by Beilstein a. Kuhlberg (*Ann. Ch. Pharm.* cxlvi. 317). 1. *Trichlorotoluene*, $C^6H^2Cl^3.CH^3$, is easily obtained by passing chlorine into toluene mixed with iodine, till 100 pts. by weight of the toluene have increased to 215·5 pts. According to Limpricht (*Ann. Ch. Pharm.* cxxxix. 303), it is also found, together with benzotrichloride, and probably also with the other two modifications above mentioned, in the product resulting from the action of chlorine alone upon toluene, and separates in crystals when the portion of the chlorinated product which boils at 230°–240° is exposed to a low temperature. When recrystallised from ether it forms long vitreous prisms which melt and solidify again at 75° to 76°; boils without decomposition at 237°, and is not altered by prolonged heating with water to 200°–220° (Limpricht). By oxidation with chromic acid it is converted into paratrichlorobenzoic (trichlorodracylic) acid (Janasch, *Jahresb.* 1867, p. 660).—2. *Dichlorobenzyl-chloride*, $C^6H^3Cl^2.CH^2Cl$, is obtained by passing chlorine into benzyl chloride, $C^6H^5.CH^2Cl$, mixed with iodine, or more readily by treating dichlorotoluene, $C^6H^3Cl^2.CH^3$, with chlorine at the boiling heat. It boils without decomposition at 241°, and contains a loosely combined chlorine-atom, replaceable by double decomposition; thus when heated with an alcoholic solution of potassium acetate, it yields potassium chloride and paradichlorobenzyl acetate, $C^6H^3Cl^2.CH^2(C^2H^3O^2)$ (Beilstein a. Kuhlberg).—3. *Chlorobenzylene chloride* (chlorinated bitter almond oil), $C^6H^4Cl.CHCl^2$, is produced when chlorine is passed into benzylene chloride (chlorobenzol or chloride of bitter almond oil) mixed with iodine, or more readily by the action of chlorine on monochlorotoluene, $C^6H^4Cl.CH^3$, at the boiling heat (Beilstein a. Kuhlberg); also by the action of phosphorus pentachloride on dichlorocresol, $C^6H^4(OH).CHCl^2$ (L. Henry, *Zeitschr. f. Chem.* [2] v. 371). Boils at 234° (B. and K.); at 227°–230°, and has a sp. gr. of 1·4 at 9° (Henry). It is decomposed by water at 170°, with formation of parachlorobenzoic aldehyde, $C^6H^4Cl.CHO$ (chlorosalicylol, according to Henry), and is oxidised by chromic acid to parachlorobenzoic acid, $C^6H^4Cl.CO^2H$ (Beilstein a. Kuhlberg).—4. *Benzotrichloride*, $C^6H^5.CCl^3$, is easily obtained quite pure by passing chlorine into boiling toluene as long as the product continues to increase in weight (100 pts. toluene take up 112·5 pts. chlorine). It boils constantly at 213°–214°, and is decomposed by water at 150°, with formation of benzoic acid:

$$C^6H^5.CCl^3 + 2H^2O = 3HCl + C^6H^5.COHO.$$

Benzoic acid is also formed, together with chlorobenzoic acid as a secondary product, when benzotrichloride is oxidised by chromic acid (Beilstein a. Kuhlberg). *Nitrobenzotrichloride*, $C^6H^4(NO^2).CCl^3$, appears to be formed by the action of fuming nitric acid on benzotrichloride, but is immediately decomposed by water into hydrochloric and nitrobenzoic acids. *Nitrobenzylene chloride*, $C^6H^4(NO^2).CHCl^2$, is formed on dropping benzylene chloride (chlorobenzol), prepared from bitter almond oil, into fuming nitric acid, as a heavy oil which cannot be obtained in the pure state; by oxidation with chromic acid it is converted into nitrobenzoic acid (Beilstein a. Kuhlberg).

Tetrachlorinated Toluenes. $C^7H^4Cl^4$.—This formula includes four possible modifications, viz.,

$C^6HCl^4.CH^3$	$C^6H^2Cl^3.CH^2Cl$	$C^6H^3Cl^2.CHCl^2$	$C^6H^4Cl.CCl^3$
Tetrachorotoluene.	Trichlorobenzyl chloride.	Dichlorobenzylene chloride.	Monochlorobenzotrichloride.

The first and fourth of these bodies, mentioned in vol. v. p. 856, have lately been further studied, together with the other two, by Beilstein a. Kuhlberg (*Zeitschr. f. Chem.* [2] iv. 276).

1. *Tetrachlorotoluene*, $C^6HCl^4.CH^3$, is formed by the prolonged action of chlorine on toluene mixed with iodine, 100 pts. toluene increasing thereby in weight to 250 pts. It is separated by fractional distillation and purified by crystallisation from absolute alcohol. It is very stable; boils without decomposition at 270°; melts at 92°–95°; is slowly acted upon by fuming nitric acid.—2. *Trichlorobenzyl chloride*, $C^6H^2Cl^3.CH^2Cl$, is easily produced by treating trichlorotoluene with chlorine at the boiling heat, 100 pts. taking up 17·6 pts. chlorine. It is a liquid boiling without decomposition at 273°; *one* of its chlorine-atoms is easily replaced by double decomposition; thus when boiled with alcoholic potassium acetate, it easily yields *trichlorobenzyl acetate*, with separation of KCl.—3. *Dichlorobenzylene chloride*, $C^6H^3Cl^2.CHCl^2$, is formed by the action of chlorine on dichlorotoluene at the boiling heat, 100 pts. increasing in weight by 43 pts. Liquid; boils without decomposition at 257°. Easily exchanges *two* of its chlorine-atoms; thus when heated with water in a sealed tube it yields hydrochloric acid, and a substance capable of uniting with acid

sodium sulphite, evidently the aldehyde of paradichlorobenzoic acid. By oxidation with chromic acid, it yields *paradichlorobenzoic acid*:

$$C^6H^3Cl^2.CHCl^2 + O + H^2O = 2HCl + C^6H^3Cl^2.CO^2H.$$

4. *Monochloro-benzotrichloride*, $C^6H^4Cl.CCl^3$, obtained by passing chlorine into benzotrichloride, is a liquid boiling without decomposition at 245°. When heated with water to 190°, it is completely resolved into hydrochloric acid and *parachlorobenzoic acid*, showing that the *three* chlorine-atoms in the methyl of the toluene molecule have exerted no influence on the position of the chlorine in the phenyl:

$$C^6H^4Cl.CCl^3 + 2H^2O = 3HCl + C^6H^4Cl.CO^2H.$$

Pentachlorinated Toluenes.—The empirical formula $C^7H^3Cl^5$ likewise admits of four modifications, viz.,

$C^6Cl^5.CH^3$	$C^6HCl^4.CH^2Cl$	$C^6H^2Cl^3.CHCl^2$	$CH^3Cl^2.CCl^3$
Pentachloro-toluene.	Tetrachloro-benzyl chloride.	Trichloro-benzylene chloride.	Dichlobenzotri-chloride.

1. *Petachlorotoluene*, $C^6Cl^5.CH^3$, is prepared by passing chlorine into toluene mixed with iodine as long as it is absorbed, the absorption being ultimately assisted by a gentle heat; then fractionating; and purifying the portion which boils at about 300° by washing with cold carbon bisulphide (which dissolves tetrachlorotoluene easily, but pentachlorotoluene with difficulty), and recrystallising from benzene. Crystallises in shining white slender needles; melts at 218°, and boils at about 300°. Very stable, not being acted on by fuming nitric acid at boiling heat.—2. *Tetrachlorobenzyl chloride*, $C^6HCl^4.CH^2Cl$, is produced by treating tetrachlorotoluene with chlorine at the boiling heat, 100 pts. increasing in weight by 15 pts. It is a liquid, boiling without decomposition at 296°-297°, and easily exchanging *one* of its chlorine-atoms, yielding, for example, tetrachlorobenzyl acetate when heated with alcoholic potassium acetate. Treated at its boiling heat with chlorine, it is converted into pentachlorobenzene, C^6HCl^5 (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2] v. 527).—3. *Trichlorobenzylene chloride*, $C^6H^2Cl^3.CHCl^2$, is prepared by treating trichlorotoluene with chlorine at the boiling heat, 100 pts. taking up 36 pts. Liquid, boiling without decomposition at 285°.—4. *Dichlorobenzotrichloride*, $C^6H^3Cl^2.CCl^3$, is produced by passing chlorine into benzotrichloride at the boiling heat as long as it is absorbed. It is a liquid, boiling without decomposition at 277°, and easily exchanging *three* of its chlorine-atoms: thus when heated with water it yields paradichlorobenzoic acid (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2] iv. 277).

Hexchlorinated Toluenes (Beilstein a. Kuhlberg, *ibid.* 561).—The formula $C^7H^2Cl^6$ admits of the three following modifications:

$C^6Cl^5.CH^2Cl$	$C^6HCl^4.CHCl^2$	$C^6H^2Cl^3.CCl^3$
Pentachlorobenzyl chloride.	Tetrachlorobenzylene chloride.	Trichlorobenzotri-chloride.

1. *Pentachlorobenzyl chloride*, $C^6Cl^5.CH^2Cl$, is prepared by passing chlorine into benzyl chloride, $C^6H^5.CH^2Cl$, mixed with iodine, as long as it continues to increase in weight, washing the product with potash, then adding a few grams of antimony trichloride, and finally passing chlorine into the moderately heated mixture as long as it continues to be absorbed. The antimony chloride is then removed by washing with strong hydrochloric acid, and the expressed product is purified by recrystallisation from alcohol and benzol. It is also produced by the prolonged action of chlorine on pentachlorotoluene at the boiling heat. Crystallises in white shining slender needles; melts at 107°–109°; boils without decomposition at about 325°; dissolves sparingly in absolute alcohol, easily in benzol. By alcoholic potassium acetate at 200°, it is converted into *pentachlorobenzyl alcohol*, $C^6Cl^5.CH^2OH$. Decomposed also by an alcoholic solution of hydropotassic sulphide.

2. *Tetrachlorobenzylene chloride*, $C^6HCl^4.CHCl^2$, is obtained by passing chlorine into tetrachlorotoluene, $C^6HCl^4.CH^3$, at the boiling heat, as long as it continues to be absorbed, and purified by fractional distillation. It is a liquid of sp. gr. 1·704 at 25°, boiling without decomposition at 305°-306°. By heating with water to 280°, it is resolved into hydrochloric acid and *tetrachlorobenzaldehyde*:

$$C^6HCl^4.CHCl^2 + H^2O = 2HCl + C^6HCl^4.CHO.$$

3. *Trichlorobenzo-trichloride*, $C^6H^2Cl^3.CCl^3$, prepared in like manner from trichlorotoluene, forms colourless, highly lustrous needles, soluble in alcohol; boils at 297°-298°; melts at 82°, and solidifies to a mass exhibiting patterns like frost-crystals. Heated with water to 250°-260°, it is easily converted into *paratrichlorobenzoic acid*:

$$C^6H^2Cl^3.CCl^3 + 2H^2O = 3HCl + C^6H^2Cl^3.CO^2H.$$

In the preparation of the compound $C^6H^2Cl^3.CCl^3$ there is likewise obtained a liquid boiling at 240°-250°, and depositing crystals which melt only at 139°. These crystals, which dissolve with difficulty both in absolute alcohol and in a mixture of alcohol and benzene, consist of tetrachlorobenzene, $C^6H^2Cl^4$ (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2] v. 529).

Heptachlorotoluenes (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2] v. 75).—The formula C^6HCl^7 admits of only two modifications, viz.,

$$C^6HCl^4.CCl^3 \text{ and } C^6Cl^5.CHCl^2.$$

Tetrachloro-benzotrichloride, $C^6HCl^4.CCl^3$, is formed by the action of chlorine on tetrachlorotoluene at the boiling heat. It is not possible, however, to convert the whole of the tetrachlorotoluene into the heptachlorinated compound, the product being a mixture of $C^6HCl^4.CH^2Cl$, $C^6HCl^4.CHCl^2$, and $C^6HCl^4.Cl^3$, which may be approximately separated by fractional distillation. The portions boiling between 310° and 320° solidify after a while; they are freed from adhering oil (consisting of the penta- and hex-chlorinated compounds just mentioned) and purified by crystallisation from alcohol.

Tetrachloro-benzotrichloride thus obtained forms dazzling white crystals; from alcoholic solution it separates by rapid cooling in short needles; by slow cooling in laminæ Boils with slight decomposition at 316°; melts at 104°. Moderately soluble in hot, slightly in cold absolute alcohol. By heating with water to 270°, it is slowly resolved into hydrochloric and para-tetrachlorobenzoic acids:

$$C^6HCl^4.CCl^3 + 2H^2O = 3HCl + C^6HCl^4.CO^2H.$$

It is not acted upon by bromine, or under the ordinary pressure by antimonic chloride.

Pentachloro-benzylene chloride, $C^6Cl^5.CHCl^2$, is not formed by the action of chlorine on pentachlorotoluene at the boiling heat, but may be prepared by treating benzylene chloride, $C^6H^5.CHCl^2$, with chlorine in presence of iodine, as long as absorption goes on, ultimately with the assistance of antimonic chloride, which, however, must not be added till every trace of iodine has been removed. The washed product is distilled, and the red distillate is washed with aqueous potash and again distilled till a colourless distillate is obtained, which is again to be mixed with antimonic chloride and treated with chlorine as long as that gas is absorbed. The antimony chloride is then removed with hydrochloric acid; the liquid distilled; the distillate mixed with a large excess of antimonic chloride and slowly redistilled; and the portions which go over after the antimonic chloride are washed with hydrochloric acid, and then repeatedly boiled with alcohol of 80 p. c., which dissolves the compound $C^6Cl^5.CHCl^2$, and leaves undissolved another heptachlorinated compound, to be presently noticed. The crystals which separate from the alcoholic solution are purified by repeated crystallisation from alcohol, whereby the compound $C^6Cl^5.CHCl^2$ is obtained in dazzling white, flat, elongated or triangularly acuminated laminæ. It melts at 109°-110°, boils constantly and without decomposition at 333°-335°; is *not* altered by heating with water to 300°, or by bromine.

Iodotoluene, $C^6H^4I.CH^3$, is obtained by decomposing sulphate of diazotoluene with hydriodic acid, washing the product with potash-ley and water, and subsequent distillation. The iodotoluene thus prepared from diazotoluene obtained by the action of nitrous acid on ordinary toluidine, forms shining laminæ, melting at 35°, boiling without decomposition at 211·5°, subliming at ordinary temperatures, and converted by oxidation with chromic acid into para-iodobenzoic acid: hence it consists of para-iodotoluene (W. Körner, *Bull. Acad. Belg.* 1867, p. 157; *Jahresb.* 1867, p. 665); but the iodotoluene obtained in like manner from the diazotoluene produced from Rosenstiehl's pseudotoluidine is liquid at ordinary temperatures, and is converted by oxidation with chromic acid mixture into ortho-iodobenzoic acid: hence it consists of ortho-iodotoluene (Körner, *Zeitschr. f. Chem.* [2] v. 636).

Nitrotoluenes. *Mononitrotoluene*, $C^6H^4(NO^2).CH^3$, was originally obtained as a liquid (i. 574); but Jaworsky (v. 858) and Kekulé (*Zeitschr. f. Chem.* [2] iii. 225) have shown that when this liquid nitrotoluene (prepared by the action of fuming nitric acid on coal-tar toluene) is subjected to fractional distillation, the greater part passes over from 220°-225°, and only the portion boiling above 233° yields pure nitrotoluene, which boils at 237°-238°, and solidifies in well-defined crystals melting at 54°. On the other hand, Beilstein a. Kuhlberg have shown that by heating dinitrotoluene (i. 575) with hydrogen, or by boiling sulphate of paradiazonitrotoluene with absolute alcohol, a liquid mononitrotoluene is obtained which does not solidify, and that the product commonly called nitrotoluene is a mixture of this liquid nitrotoluene with the solid modification. When nitrotoluene is prepared by adding nitric acid (sp. gr. 1·475) to cooled toluene, and the product is subjected to fractional distillation at intervals of 2°, we obtain, after fifteen to twenty distillations, two portions, one boiling between 222° and 223°, the other between 235° and 236°, the portions of intermediate boiling point being quite insignificant. That which passes over above 230° solidifies for the most part very quickly by separation of solid nitrotoluene; the portion of lower boiling point does not solidify. The liquid nitrotoluene obtained in the manner just described is identical in physical and chemical properties with that obtained from dinitrotoluene; prepared in either way it boils at 222°–223°, and has a specific gravity of 1·162–1·163 at 23°. The sulpho-acids, toluidines and acetotoluides, prepared from liquid nitrotoluene obtained in either way, likewise agree in their properties, but differ widely from the corresponding derivatives of solid nitrotoluene. For example, toluidine obtained from liquid nitrotoluene is also a liquid which does not solidify, and boils at 199°, whereas toluidine from solid nitrotoluene is crystalline, melts at 45°, and boils at 200° (*Zeitschr. f. Chem.* [2] v. 521).

Ammonium sulphite acts on nitrotoluene in the same manner as on nitrobenzene (p. 268), forming disulphuryl-tolnylic acid, $C^7H^9NS^2O^6$ (Carius, *Jahresb.* 1861, p. 635).

Nitrobenzyl chloride, $C^6H^4(NO^2).CH^2Cl$, produced by dissolving benzyl chloride in fuming nitric acid, and freed from an oily body formed at the same time, by pressure and recrystallisation from alcohol, forms laminar crystals melting at 71°. By oxidation with chromic acid it is easily converted into paranitrobenzoic acid (Beilstein a. Geitner, *Ann. Ch. Pharm.* cxxxix. 331). According to Grimaux (*Bull. Soc. Chim.* [2] viii. 433), this compound melts at 73°, remains liquid till cooled to 60°, and then solidifies suddenly when touched, the temperature rising to 69°. Heated with alcoholic solution of potassium acetate, it is converted into nitrobenzyl acetate, $C^6H^4(NO^2).CH^2(C^2H^3O^2)$, which dissolves sparingly in boiling water, easily in alcohol and ether, and crystallises therefrom in thin shining laminæ, melting at 85°. Benzyl acetate treated with fuming nitric acid yields a thick oil from which a white solid body may be separated.

Reduction-derivatives of Nitrotoluene.

Amidotoluene. $C^6H^4(NH^2).CH^3$.—See TOLUIDINE (v. 865, and in this volume).

Diazotoluene. $C^7H^6N^2$.—See AZOTOLUIDINE (v. 867).

Azotoluene. $C^{14}H^{14}N^2$. *Azotoluol. Azotoluid* (Werigo, *Zeitschr. Ch. Pharm.* 1864, pp. 481, 721; Jaworsky, *ibid.* 640).—Produced by the action of sodium-amalgam on nitrotoluene dissolved in aqueous alcohol. On acidulating with acetic acid and removing the unaltered nitrotoluene by distillation, the azotoluene remains as a soft red mass, which, after washing with cold and recrystallisation from hot alcohol, is obtained in shining orange-red needles. It melts at 137°, sublimes without decomposition, is insoluble in water, dilute acids and alkalis, but dissolves in strong sulphuric acid, and is precipitated therefrom by water. By the further action of sodium-amalgam, it is converted into hydrazotoluene, $C^{14}H^{16}N^2$.

Azotoluene, like azobenzene, unites directly with *bromine*, forming the compound $C^{14}H^{14}N^2Br^2$; but when bromine is added to a solution of azotoluene (such as that obtained in its preparation), a crystalline precipitate is formed, which after recrystallisation, with addition of animal charcoal, forms white shining laminæ. This body has the composition $C^{14}H^{20}N^2Br^4$, and has one half of its bromine more intimately combined than the other half. It may be regarded as the *tetrahydrobromide of hydrazotoluene*, $C^{14}H^{16}N^2.4HBr$, or as the dihydrobromide of the diamine $C^{14}H^{18}Br^2N^2$. It dissolves in water and in alcohol, but not in ether; sublimes without residue in white needles; decomposes above 100°, with formation of red vapours; reacts strongly acid in aqueous solution; and forms with ammonia or soda a precipitate soluble in excess of the reagent. With *chlorine*, azotoluene forms the analogous compound $C^{14}H^{20}N^2Cl^4$.

On mixing a hot concentrated aqueous solution of the bromine-compound $C^{14}H^{20}N^2Br^4$ with a quantity of silver nitrate equivalent to half the bromine, the solution, after removal of the precipitated silver bromide, yields long needle-shaped crystals, soluble in water and alcohol, but not in ether, and consisting of the *nitrate* $C^{14}H^{18}Br^2N^2.2NO^3H$. The aqueous solution of the bromine-compound $C^{14}H^{20}N^2Br^4$ forms with caustic soda a white crystalline precipitate, which, after reprecipitation from alcoholic solution by water, forms long colourless needles, easily soluble in alcohol and ether, but only slightly in water. This compound is neutral, melts at 57·5°, and consists of $C^{14}H^{18}N^2Br^2$ (Werigo, *Zeitschr. f. Chem.* 1865, p. 631; 1866, p. 196; *Jahresb.* 1866, p. 465).

Nitrazotoluenes.—Nitric acid of sp. gr. 1·5, gradually added to cooled azotoluene, converts it almost wholly into mononitrazotoluene, $C^{14}H^{13}(NO^2)N^2$, which crystallises from alcohol in two forms—first in reddish needles melting at 67°, afterwards in small yellow crystals melting at 63°. When, on the other hand, crystals of azotoluene are gradually added to strong nitric acid without cooling, two other bodies are formed, viz.: (1) *Trinitrazotoluene*, $C^{14}H^{11}(NO^2)^3N^2$, which dissolves with moderate facility in hot alcohol, and separates on cooling in thin yellow needles sparingly soluble in ether, and melting at about 185°.—(2) *Trinitrazoxytoluene*, $C^{14}H^{11}(NO^2)^3N^2O$, nearly insoluble in alcohol, but soluble in nitric acid and in benzol, and separating therefrom in sulphur-yellow crystals melting at 201°, and decomposing at a higher temperature with explosion and separation of charcoal (Petrieff, *Zeitschr. f. Chem.* [2] vi. 264).

Azoxytoluene, $C^{14}H^{14}N^2O$, is obtained, together with azotoluene, by the action of sodium-amalgam on nitrotoluene in alcoholic solution, and separates from the alcoholic mother-liquor in the form of a red oil (Jaworsky, *Jahresb.* 1864, p. 527). Petrieff (*Zeitschr. f. Chem.* [2] vi. 30) has more recently obtained it in red crystalline laminæ melting at 57°, more soluble in alcohol than azotoluene, and therefore remaining in the mother-liquor after the latter has separated. By the further action of sodium-amalgam it is reduced to hydrazotoluene, $C^{14}H^{16}N^2$.

SULPHO-DERIVATIVES OF TOLUENE.

Toluene-sulphuric Acid. $C^7H^7.SO^3H$ (Engelhardt a. Latschinoff, *Zeitschr. f. Chem.* [2] v. 617).—Toluene heated with sulphuric acid yields two isomeric sulpho-acids. To prepare them, 500 grms. of pure toluene are heated for two days in the water-bath with an equal volume of fuming sulphuric acid; the resulting mass is dissolved in water and neutralised with lime; the filtered solution is freed from excess of sulphuric acid by barium hydrate; the excess of lime and baryta precipitated by carbonic acid; the filtered solution decomposed by potassium carbonate; and the solution of the potassium salts concentrated by evaporation. This solution, not too concentrated, deposits on slow cooling two potassium salts, α and β, sharply distinguished from one another by their crystalline forms; the former separating in large prismatic crystals; the latter, which is the more soluble of the two, in loose nodular groups of slender needles. They crystallise together, but may be mechanically separated by a sieve, the α salt remaining thereon, while the β salt passes through with the mother-liquor. The α salt is easily purified by recrystallisation from water; but the β salt can only be approximately purified by several crystallisations, first from water, afterwards from alcohol. To prepare the other salts of these two acids, the potassium salts are decomposed by sulphuric acid, and the separated acids are dissolved out by alcohol and neutralised with barium carbonate, &c.

α *Toluene-sulphates.*—The *potassium salt* $C^7H^7SO^3K.H^2O$ dissolves easily in hot water, and crystallises by slow cooling of the moderately concentrated solution, in beautiful elongated, six-sided tables, or long prisms resembling saltpetre; from highly concentrated solutions in long needles. It is soluble in hot alcohol, and crystallises therefrom in needles. The crystals effloresce in the air. The *sodium salt* crystallises from alcohol in shining laminæ. The *barium salt* $(C^7H^7SO^3)^2Ba$ is easily soluble in boiling water, and crystallises on cooling in shining laminæ. The *calcium salt* crystallises from alcohol in needles.

β *Toluene-sulphates.*—The *potassium salt* $2C^7H^{\cdot}SO^3K.3H^2O$ is very soluble in water and in boiling alcohol, and crystallises from the former in nodular groups of slender needles, from the latter in shining laminæ. The *barium salt* $(C^7H^7SO^3)^2Ba.H^2O$ is easily soluble in boiling water and crystallises in white nodules.

ORTOBROMOTOLUENE-SULPHURIC ACID, $C^6H^3CH^3Br.SO^3H$, is produced by heating toluene bisulphoxide with excess of bromine in sealed tubes and remains on evaporation as a yellow mass. Its barium salt, $(C^6H^3CH^3BrSO^3)^2Ba.2H^2O$, forms beautiful laminæ, very slightly soluble in water, and sustaining a heat of 200° without decomposition (Otto, Löwenthal a. Gruber, *Zeitschr.* [2] iv. 626). The *calcium salt* $(C^6H^3CH^3BrSO^3)^2Ca.3H^2O$ crystallises from water in slender needles, which have a great tendency to creep over the sides of the vessel. When slowly crystallised from alcohol or water it forms thick, often crossed needles, having a silky lustre (Hübner a. Wallach, *ibid.* 502).

METABROMOTOLUENE-SULPHURIC ACID. $C^6H^3BrCH^3.SO^3H$.—Hübner a. Wallach (*Zeitschr. f. Chem.* [2] v. 500) describe two modifications of this acid—the one obtained from fluid, the other from crystallised bromotoluene; they may be distinguished by the prefixes *f* and *c*.

f Metabromotoluene-sulphuric acid is easily produced by dissolving liquid bromotoluene in fuming sulphuric acid; it salts crystallise well; the *calcium salt*

$(C^7H^6BrSO^3)^2Ca.1\frac{1}{2}H^2O$ in tufts of delicate crystals which give off their water at 100°. The *sodium salt* $C^6H^6BrSO^3Na$ crystallises from water in nodular groups of needles, from alcohol in transparent laminæ. The crystals contain water, which escapes so easily that its amount could not be determined.

c Metabromotoluene-sulphuric acid, prepared from solid bromotoluene, crystallises from water or ether in very small colourless needles or plates, which appear oblique-angled under the microscope. A very concentrated solution of solid bromotoluene in fuming sulphuric acid, mixed with a small quantity of water, deposits the acid on cooling in small shining laminæ. The *lead salt* of this acid, $(C^6H^3BrCH^3SO^3)^2Pb$, crystallises in furcate groups of long transparent needles, which in thick layers appear opaque and exhibit a fine satiny lustre. The *sodium salt*, crystallised from alcohol, forms small needles, passing by slower crystallisation into large very thin plates; they also give off their water of crystallisation too easily to allow of its exact determination.

f Metabromotoluene-sulphochloride, $C^6H^3BrCH^3.SO^2Cl$, is produced by heating the sodium salt of the corresponding sulpho-acid with phosphorus pentachloride. On adding water to the product the sulphochloride separates as a light brown fetid oil, which does not solidify even in a freezing mixture. It dissolves easily in alcohol.

c Metabromotoluene-sulphochloride from solid bromotoluene, does not differ sensibly from the compound just described.

Chlorotoluene-sulphuric acid, $C^7H^6Cl.SO^3H$, is formed, as above mentioned, by the action of chlorine on toluene bisulphoxide suspended in water, and remains on evaporation as a colourless syrup, gradually crystallising over oil of vitriol. The *barium salt* of this acid crystallises in splendid shining flat needles, almost an inch long, very slightly soluble in cold water, and consisting of $(C^7H^6ClSO^3)^2Ba.2H^2O$ (Otto, Löwenthal a. Gruber).

1. **Nitrotoluene-sulphuric or Sulphonitrotoluolic Acid.** $C^7H^6(NO^2).SO^3H$.—This acid has been supposed to exhibit two modifications, accordingly as it is prepared on the one hand by the action of sulphuric acid on nitrotoluene (Jaworsky), or on the other by the oxidation of metabenzylsulphydrate with nitric acid (Märcker), or by the action of fuming nitric acid on toluene-sulphurous acid (Otto); see vol. v. p. 860. These acids have been further examined by Engelhardt a. Bek (*Zeitschr. f. Chem.* [2] v. 209) with the following results: (1) The *barium salt* of Jaworsky's acid has the same composition as that of Märcker's acid, viz. $[C^7H^6(NO^2)SO^3]^2Ba.2H^2O$. This salt is sparingly soluble in cold water.—(2) In the action of nitric acid on toluene-sulphurous acid, there is obtained, as principal product, a nitrotoluene-sulphuric acid, not differing in any essential particular from the acid obtained from nitrotoluene.—(3) The nitro-acid obtained from either source yields, by reduction with hydrogen sulphide, one and the same amidotoluene-sulphuric acid, which is different from the two sulpho-acids obtained by the action of sulphuric acid upon toluidine (p. 288). (4) The action of nitric acid on toluene-sulphurous acid likewise yields, as a secondary product, another nitro-acid, which, when reduced by hydrogen sulphide, yields an amidated acid very similar to the toluidine-sulphuric acids just mentioned. The *barium salt* of this nitro-acid, which was not obtained pure, remains in solution after the above-mentioned sparingly soluble barium salt has crystallised out.

Nitrotoluene-sulphochloride, $C^7H^6(NO^2)SO^2Cl$, produced by the action of 1 mol. phosphorus pentachloride on 1 mol. sodium nitrotoluene-sulphate, is a yellowish oil, insoluble in water, but easily soluble in alcohol and ether, and is decomposed by alkalis, with formation of nitrotoluene-sulphuric acid (Otto a. v. Gruber, *Jahresb.* 1867, p. 678).

Nitrotoluene-sulphamide or *Nitrosulphotoluolamide*, $C^7H^8(NO^2)NSO^2$, produced by the action of ammonia on the sulphochloride, crystallises in four-sided rhombic prisms or long needles, which melt at 120°, and dissolve readily in hot water and alcohol (Otto a. v. Gruber).

2. **Amidotoluene-sulphuric acid**, $C^7H^7(NH^2)SO^3$, is prepared by saturating the solution of ammonium nitrotoluene-sulphate in ammonia with hydrogen sulphide, boiling the solution to expel the excess of ammonium sulphide, mixing the filtered liquid with hydrochloric acid at the boiling heat, again concentrating, and filtering to separate any sulphur that may still be present. On cooling, the amidated acid separates in slightly coloured prismatic crystals, which may be purified by treatment with animal charcoal and recrystallisation. Amidotoluene-sulphuric acid is sparingly soluble in cold, more easily in boiling water, almost insoluble in alcohol, and crystallises from the aqueous solution by slow cooling, in long shining four-sided prisms with end-faces, by rapid cooling in needles, the crystals in both cases containing

$C^7H^7(NH^2)SO^3.H^2O$. The acid decomposes carbonates, and its solutions have a strong acid reaction. Its salts are easily soluble in water and crystallise well. On adding silver nitrate to the solution of an amidotoluene-sulphate, and heating to the boiling point, metallic silver separates, and the solution turns violet. The *barium salt* $2[C^7H^6(NH^2)SO^3]^2Ba.5H^2O$ crystallises in beautiful tables; the *calcium salt* $[C^7H^6(NH^2)SO^3]^2Ca.2H^2O$, in shining six-sided tables; the *potassium salt* $C^7H^6(NH^2)SO^3K.H^2O$ is easily soluble in water; the *sodium salt* $C^7H^6(NH^2)SO^3Na.4H^2O$ crystallises from a boiling alcoholic solution in shining flat needles.

The ammonium salt of the nitrotoluene-sulphuric acid corresponding to the easily soluble barium salt above mentioned, yields in like manner by reduction with hydrogen sulphide, a small quantity of an amidotoluene-sulphuric acid which crystallises in rhombic tables, and closely resembles β-sulphotoluidic acid (Engelhardt a. Beck).

TOLUIDINE-SULPHURIC OR SULPHOTOLUIDIC ACID. $C^7H^9NSO^3$ (Malyscheff, *Zeitschr. f. Chem.* [2] v. 212).—An acid of this composition (sulphotolylamic acid) was obtained by Sell (v. 527) by heating toluidine with fuming sulphuric acid, together with another acid which he regarded as toluidine-disulphuric (benzyldisulphamic) acid. Malyscheff has found, however, that the two acids thus obtained are isomeric, both having the composition $C^7H^9NSO^3$, and being likewise isomeric with Bek's amidotoluene-sulphuric acid.

In preparing these acids it is of special importance to regulate the heat carefully, as if it rises too high, the mass chars, and if the heat is insufficient, nothing but toluidine sulphate is obtained. The product of the properly conducted action is a black thick liquid, which, when diluted with water and left to itself, deposits a black crystalline mass, to be decolorised by solution in boiling water and treatment with animal charcoal. The solution filtered at the boiling heat deposits on cooling slender needles of *α-toluidine-sulphuric acid* and large well-defined rhombic plates of *β-toluidine-sulphuric acid*, which may be separated from one another, first by levigation—the α-acid being carried away by the water more easily than the β-acid—and finally by recrystallisation, the α-acid dissolving more readily than the β-acid when hot water is poured upon the mixed crystals of the two.

α Toluidine-sulphuric acid, $C^7H^9NSO^3.1\frac{1}{2}H^2O$ (air-dried), the acid described by Sell, crystallises in slender light yellow needles, which cannot be completely decolorised by animal charcoal; it is moderately soluble in cold, more easily in boiling water. The *barium salt* $5(C^7H^8NSO^3)^2Ba.8H^2O$ dissolves easily in boiling water, somewhat less easily in cold water, and crystallises from a hot solution on cooling in beautiful shining plates, which do not give off their water over oil of vitriol. The *silver salt* $C^7H^8NSO^3Ag$ forms colourless shining laminæ. The *potassium salt* $C^7H^8NSO^3K.\frac{1}{2}H^2O$ crystallises in needles or in elongated six-sided plates, very soluble in boiling, somewhat less in cold water and alcohol.

β Toluidine-sulphuric acid, $C^7H^9NSO^3.H^2O$, is formed in larger quantity than the α-acid in the process above described. It is very slightly soluble in cold, moderately soluble in boiling water, and crystallises in fine large shining rhombic plates, which are commonly yellowish, but may be decolorised by animal charcoal. The aqueous solution has an acid reaction and dissolves carbonates, with evolution of carbon dioxide. The salts of the β-acid are easily soluble in water; the solutions, when evaporated over the water-bath, decompose partially and turn red. On adding *silver nitrate* to the ammoniacal solution of the β-acid, and warming, silver separates in the specular form, and the liquid acquires a violet-red colour.

Potassium salt,	$C^7H^8NSO^3K$,	shining six-sided laminæ.
Ammonium ,,	———	colourless laminæ.
Barium ,,	$(C^7H^8NSO^3)^2Ba.3H^2O$,	shining laminæ.
Lead ,,	$(C^7H^8NSO^3)^2Pb$,	crystalline powder.

Toluene-sulphurous Acid. $C^7H^8SO^2 = C^7H^7.SO^2H$.—The following additional observations on this acid have been made by Otto a. v. Gruber (*Ann. Ch. Pharm.* cxlv. 10; *Jahresb.* 1867, p. 678). A mixture of this acid with phosphorus pentachloride in equivalent quantities forms, with violent action, a liquid mass, which solidifies on cooling, and when treated with water yields (together with a small quantity of an oily product) toluene-sulphochloride, $C^7H^7SO^2Cl$, melting after recrystallisation from ether at 69°–70°. Toluene-sulphurous acid is not acted upon by sodium-amalgam in alkaline solution; heated with water to 130°, it is resolved into oxybenzyldisulphide and toluene-sulphuric acid:

$$3C^7H^8SO^2 = C^{14}H^{14}S^2O^2 + C^7H^8SO^3 + H^2O.$$

Heated to 300° with potassium hydrate, it is resolved into potassium sulphite and toluene:

$$C^7H^7KSO^3 + KHO = SO^3K^2 + C^7H^8.$$

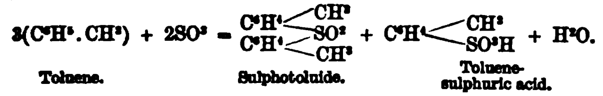
From a solution of toluene-sulphurous acid in fuming nitric acid, a compound $C^{21}H^{22}N^2S^3O^6$, called diazotrisulphotoluene hydride, is precipitated, whilst nitrotoluene-sulphuric acid, $C^7H^7(NO^2)SO^3$, remains in solution. The diazo-compound is insoluble in water, slightly soluble in hot alcohol, easily in benzol, and crystallises from the latter in white hard rhombic tablets, melting at 190°. The same compound is produced by the prolonged action of nitrous acid on an aqueous or alcoholic solution of toluene-sulphurous acid, its formation in this latter case being preceded by that of another azotised body of lower melting point, which crystallises out first on cooling. The formation of diazotrisulphotoluene hydride is represented by the equations,

$$\underset{\substack{\text{Toluene-}\\\text{sulphurous acid.}}}{5C^7H^8SO^2} + 4NO^2 = \underset{\substack{\text{Diazotrisulpho-}\\\text{toluene hydride.}}}{C^{21}H^{22}N^2S^3O^6} + \underset{\substack{\text{Nitrotoluene-}\\\text{sulphuric acid.}}}{2C^7H^7(NO^2)SO^3} + 2H^2O.$$

$$4C^7H^8SO^2 + 2N^2O^3 = C^{21}H^{22}N^2S^3O^6 + C^7H^7(NO^2)SO^3 + NHO^2 + H^2O.$$

Nitrotoluene-sulphurous Acid. $C^7H^7(NO^2)SO^2$.—The sodium salt of this acid, $C^7H^6(NO^2)SO^2Na.\frac{1}{2}H^2O$, is produced by the action of sodium-amalgam on a solution of nitrotoluene-sulphochloride in pure ether. It is easily soluble in water and in hot alcohol, and crystallises in feathery tufts of striated needles (Otto a. von Gruber).

Sulphotoluide. $C^{14}H^{14}SO^2 = C^6H^4(CH^3)-SO^2-C^6H^4(CH^3)$.—First obtained by Deville (*Ann. Ch. Pharm.* xliv. 306); further examined by Otto a. Gruber (*Zeitschr. f. Chem.* [2] vi. 33). Prepared like sulphobenzide by passing vapour of sulphuric anhydride into toluene:



$$\underset{\text{Toluene.}}{3(C^6H^5.CH^3)} + 2SO^3 = \underset{\text{Sulphotoluide.}}{\begin{matrix} & CH^3 \\ C^6H^4 & \\ & SO^2 \\ C^6H^4 & \\ & CH^3 \end{matrix}} + \underset{\substack{\text{Toluene-}\\\text{sulphuric acid.}}}{C^6H^4\begin{matrix} CH^3 \\ SO^3H \end{matrix}} + H^2O.$$

On pouring the oily mass into water, washing the precipitate with water, and crystallising from benzol, sulphotoluide is obtained in transparent clino-rhombic prisms having a vitreous lustre; from hot alcohol it crystallises in small tabular prisms. It melts at 155°–156°, is insoluble in water, slightly soluble in cold alcohol and ether, more freely in boiling alcohol and in benzol, chloroform, and carbon bisulphide. When heated in small quantities, it volatilises without decomposition. Heated with strong sulphuric acid, it dissolves as toluene-sulphuric acid. Red fuming nitric acid dissolves it without decomposition, but a mixture of this acid with sulphuric acid converts it, with aid of heat, into crystallisable nitro-derivatives. It is not altered by heating to 160° with alcoholic potash. With chlorine and phosphorus pentachloride, it appears to react like sulphobenzide, but the products are less definite and have not been thoroughly examined (Otto a. Gruber).

Tolyl Bisulphoxide. $C^{14}H^{14}S^2O^2$ (Otto, Löwenthal a. Gruber, *Zeitschr. f. Chem.* [2] iv. 623).—This compound, first obtained by Märcker (benzyl-dioxysulphide, v. 859) by oxidising toluene sulphydrate with nitric acid, was afterwards prepared by Otto a. von Gruber (*Zeitschr.* [2] iii. 600, 611) by heating toluene-sulphurous acid with water to 120°–130° in sealed tubes:

$$\underset{\substack{\text{Toluene sulphur-}\\\text{ous acid.}}}{3C^7H^8SO^2} = \underset{\substack{\text{Tolyl}\\\text{bisulphoxide.}}}{C^{14}H^{14}S^2O^2} + \underset{\substack{\text{Toluene-}\\\text{sulphuric acid.}}}{C^7H^8SO^3} + H^2O.$$

It is insoluble in water, but dissolves easily in boiling alcohol, ether, and benzol, and crystallises in large transparent glassy crystals resembling the scalenohedrons of calcspar and melting at 76° (not at 74° as stated by Märcker). By nascent hydrogen (evolved either by zinc and sulphuric acid or by sodium-amalgam) it is converted into tolyl sulphydrate: $C^{14}H^{14}S^2O^2 + 3H^2 = 2H^2O + 2C^7H^8S$. By boiling with alcoholic potash, it is converted into toluene-sulphite and toluene-sulphate of potassium, which dissolve, and toluene bisulphide (or metabenzylic bisulphide, v. 659), which remains undissolved:

$$\underset{\substack{\text{Tolyl-}\\\text{bisulphoxide.}}}{2C^{14}H^{14}S^2O^2} + H^2O = \underset{\substack{\text{Toluene-sul-}\\\text{phurous acid.}}}{C^7H^8SO^2} + \underset{\substack{\text{Toluene-sul-}\\\text{phuric acid.}}}{C^7H^8SO^3} + \underset{\substack{\text{Tolyl-}\\\text{bisulphide.}}}{C^{14}H^{14}S^2}$$

Tolyl bisulphide is not attacked by boiling potash. Fuming sulphuric acid colours it first yellow and then green in the cold, and dissolves it on warming to a deep indigo-coloured liquid which is decolorised by water.

Bromide of Tolyl Bisulphoxide. $(C^{14}H^{14}S^2O^2)^2Br^2$.—Obtained by dropping 1 at. bromine into a molecule of the bisulphoxide suspended in water, and heating the liquid to the melting point of the bisulphoxide. Small white needles insoluble in water, easily soluble in ether and in benzol. By boiling with strong aqueous ammonia, it is resolved into ammonium bromide, sulphotoluamide (v. 527), and tolyl bisulphide:

$$(C^{14}H^{14}S^2O^2)^2Br^2 + 4NH^3 = 2NH^4Br + N^2(C^7H^7SO^2)^2H^2 + C^{14}H^{14}S^2.$$

With strong aqueous potash, it yields bromide, toluene-sulphite, and toluene-sulphate of potassium, together with tolyl bisulphide, probably in two stages, the first consisting in the formation of potassium toluene-sulphite and tolyl bisulphoxide:

$$(C^{14}H^{14}S^2O^2)^2Br^2 + 4KHO = 2KBr + 2C^7H^7KSO^2 + C^{14}H^{14}S^2O^2 + 2H^2O,$$

and the second in the conversion of the bisulphoxide into toluene-sulphurous acid, toluene-sulphuric acid, and tolyl bisulphide, in the manner already explained.

Tolyl bisulphide exposed for some time under water at 100° to the action of *bromine* in excess is *oxidised* to tolyl sulphobromide (i. 859):

$$C^{14}H^{14}S^2O^2 + Br^2 + O^2 = 2C^7H^7BrSO^2.$$

Heated for an hour or two with excess of *bromine* and water in sealed tubes, it dissolves almost completely as bromotoluene-sulphuric or sulphobromotoluic acid:

$$C^{14}H^{14}S^2O^2 + Br^2 + O^4 = 2C^7H^7BrSO^3.$$

Chlorine acts on the bisulphoxide in the same manner as bromine, but more energetically. On passing the gas into water at about 80° in which tolyl bisulphoxide is suspended, long needles of tolyl sulphochloride, $C^7H^7ClSO^2$ (i. 859), melting at 68°, sublime in the stream of chlorine, and the bisulphoxide gradually dissolves, leaving only a very small residue of secondary products, while the solution contains chlorotoluene-sulphuric acid, $C^7H^7ClSO^3$.

Tolyl Sulphide, $C^{14}H^{14}S = (C^7H^7)^2S = \left.\begin{matrix}C^6H^4(CH^3)\\C^6H^4(CH^3)\end{matrix}\right\}S$, may be obtained by distilling the lead-compound of the sulphydrate, $(C^7H^7)^2PbS^2 = PbS + (C^7H^7)^2S$, and is easily purified by redistillation. It is a colourless oil, smelling like the sulphydrate, heavier than water, insoluble therein, easily soluble in absolute alcohol, ether, and benzene (Otto, Löwenthal a. v. Gruber, *loc. cit.*).

Tolyl Sulphydrate. $C^7H^8S = C^6H^4(SH).CH^3$. *Metabenzyl Sulphydrate. Cresylic Mercaptan* (v. 858).—In preparing this compound by the action of zinc and sulphuric acid on tolyl sulphochloride, the zinc often becomes enveloped by the sulphochloride in such a manner as greatly to interfere with the action. To avoid this inconvenience, it is best, first to convert the sulphochloride into the sodium salt of toluene-sulphurous acid by the action of sodium-amalgam, and distil the aqueous solution of this salt—without previous separation of sodium chloride—with zinc and dilute sulphuric acid. The process thus modified yields almost the theoretical quantity of tolyl sulphydrate. The same compound is produced by the action of nascent hydrogen on tolyl bisulphoxide (Otto, Löwenthal a. Gruber, *Zeitschr.* [2] iv. 623, 628).

Metabromotolyl Sulphydrate, $C^6H^3Br(SH).CH^3$, is obtained in two modifications—fluid (*f*) and crystalline (*c*)—by the action of nascent hydrogen on the corresponding sulphochlorides (p. 287) (Hübner a. Wallach, *Zeitschr. f. Chem.* [2] v. 500).

f Metabromotolyl Sulphydrate may be prepared by boiling the corresponding sulphochloride with zinc and sulphuric acid, but much more quickly with tin and hydrochloric acid: it may be conveniently distilled off the metallic chloride by means of a current of steam. It is a mobile liquid, of disagreeable odour, not solidifying at −20°; it may be dried over calcium chloride or potassium hydrate, and then boils, with slight decomposition, at 245°–246°. Insoluble in water, easily soluble in alcohol; dissolved by strong sulphuric acid, with fine blue colour and copious evolution of sulphurous oxide. The hydrogen-atom of the SH group is easily exchanged for metals, forming amorphous salts which are distinguished by very sparing solubility in water and for the most part also in alcohol.

f Metatolyl Sulphydrate, $C^6H^4CH^3.SH$, is produced by agitating the preceding compound for several days with sodium-amalgam. It is also a mobile oil having a pungent odour like that of the brominated compound, but stronger. Boils constantly and without decomposition at 187°–188°, and does not solidify in a freezing mixture. Towards solvents and metallic solutions it behaves like the brominated sulphydrate, but its salts are much more soluble.

c Metabromotolyl Sulphydrate prepared from the corresponding sulphochloride with tin and hydrochloric acid, boils, not quite without decomposition, at 245°, and solidifies at about 7° to a white radio-crystalline mass. Its salts resemble those of the corresponding sulphydrate obtained from liquid bromotoluene.

c Metatolyl Sulphydrate, obtained from the last compound by the action of sodium-amalgam, boils at 188° and solidifies in a freezing mixture to a splendid, perfectly uniform, colourless crystalline mass, melting at about 2°. Its salts do not differ perceptibly from those of the corresponding sulphydrate obtained from liquid bromotoluene.

The following table gives a comparative view of the physical properties of these metatolyl sulphydrates and their salts, together with those of orthotolyl sulphydrate (Märcker's metabenzyl sulphydrate, v. 858), and of benzyl sulphydrate or benzylic mercaptan:

	Benzyl sulphydrate	Orthotolyl sulphydrate	Metatolyl sulphydrate from liquid bromotoluene	Metatolyl sulphydrate from solid bromotoluene
Boiling point .	194°–195°	188°	188°	188°
Melting point		42·5° Crystallises very easily in large laminæ.	Still fluid at −20°.	+ 2 Crystallises in beautiful broad transparent needles.
Solubility .	Soluble in alcohol.	Insol. in water: sol. in alcohol; dissolving in strong sulphuric acid with splendid blue colour.		
Lead salt .	Light yellow laminæ	Orange-yellow flocks, decomposible by light.	Deep yellow; amorphous. Melts at about 70°; not altered by light; white needles with fine lustre.	Deep yellow; amorphous. Melts at 76°–78°; not altered by light; white needles with fine lustre.
Mercury salt .	Long silky needles.	White laminæ decomposible by light.	Melts at 100°; not altered by light.	Melts at 123°–126°; not altered by light.
Silver salt .	White.	Siskin-green.	Light yellow.	White (soon turning yellow).
Copper salt .	Green.	Green.	Dirty yellow.	Dirty yellow.
Reaction with nitric acid .	Yields sulphuric acid, small quantities of benzoic acid and benzoic aldehyde.	Yield small quantities of sulphuric acid.		

Hydrocarbons C^8H^{10}. Xylenes.

This formula admits of the two metameric modifications:

$C^6H^5.C^2H^5$ Ethyl-benzene
$C^6H^4.(CH^3)^2$ Dimethyl-benzene,

the second of which is further susceptible of isomeric modification, as *ortho-*, *meta-*, and *para-*, according to the relative position of the two methyl-atoms, viz. 1 : 2, 1 : 3, 1 : 4.

Ethyl-benzene. $C^6H^5.C^2H^5$.—The synthetical formation of this body by the action of sodium on a mixture of monobromobenzene and ethyl bromide has been already noticed (v. 1056). It is also produced, together with diethyl-benzene and a small quantity of benzene, by heating naphthalene for some time with 20 pts. of saturated aqueous hydriodic acid:

$$\underset{\text{Naphthalene.}}{C^{10}H^8} + 3H^2 = \underset{\text{Diethyl-benzene.}}{C^{10}H^{14}}$$

$$C^{10}H^8 + 4H^2 = \underset{\text{Ethyl-benzene.}}{C^8H^{10}} + \underset{\text{Ethane.}}{C^2H^6}$$

$$C^{10}H^8 + 5H^2 = \underset{\text{Benzene.}}{C^6H^6} + \underset{\text{Ethane.}}{2C^2H^6}$$

(Berthelot, *Bull. Soc. Chim.* [2] ix. 289.) See NAPHTHALENE. Also by heating cinnamene (styrol), C^8H^8, with 20 pts. of hydriodic acid (Berthelot, *Jahresb.* 1867, p. 349).

Ethyl-benzene is almost completely decomposed when its vapour is passed through a red-hot tube, yielding cinnamene with smaller quantities of benzene, toluene, naphthalene, and naphthalene hydride, $C^{10}H^{10}$:

$$3C^8H^{10} = 2C^7H^8 + C^{10}H^8 + 3H^2$$
$$3C^8H^{10} = 2C^7H^8 + C^{10}H^{10} + 2H^2$$

(Berthelot, *Zeitschr. f. Chem.* [2] iv. 589).

By prolonged oxidation with dilute nitric acid, or by chromic acid, ethyl-benzene is converted into benzoic acid, without previous formation of α-toluic acid (Fittig a. König, *Jahresb.* 1867, p. 609).

The *bromo-* and *nitro-*derivatives of ethyl-benzene are partly described in vol. v. pp. 1057, 1058.

Bromethyl-benzene, $C^6H^4Br(C^2H^5)$, has a sp. gr. of 1·34 at 35° and boils at 199°. By oxidation with chromic acid mixture it yields parabromobenzoic acid (Fittig a. König). By the action of carbon dioxide and sodium it is converted into ethyl-benzoic acid, isomeric with xylic (dimethyl-benzoic) acid (Kekulé, *Ann. Ch. Pharm.* cxxxvii. 178; Kekulé a. Thorpe, *Chem. Soc. J.* [2] vii. 366):

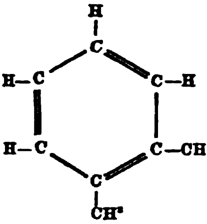
$$C^6H^4Br(C^2H^5) + Na^2 + CO^2 = NaBr + C^6H^4(C^2H^5).CO^2Na.$$

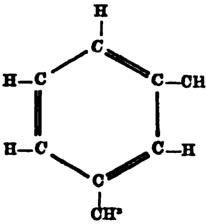
Beilstein a. Kuhlberg (*Zeitschr. f. Chem.* [2] v. 524) have recently demonstrated the existence of two modifications of *mononitro-ethyl-benzene*. When nitric acid of sp. gr. 1·475 is added to ethyl-benzene till a clear solution is formed, and the product after washing with water and ammonia, is distilled, it passes over on the first distillation at 226°–251°, and if then fractionated twenty times at intervals of 2°, separates almost entirely into two portions, viz. α and β, both of which are liquids not solidifying even in a freezing mixture. *α-nitroethylbenzene* boils at 245°–246°, has a sp. gr. of 1·124 at 25°, and is easily oxidised by chromic acid mixture yielding nitrodracylic acid. *β-nitroethylbenzene* boils at 227°–228°, has a sp. gr. of 1·126 at 24·5°, and when treated with the chromic acid mixture does not yield any acid, but if the action be continued, suffers complete combustion.

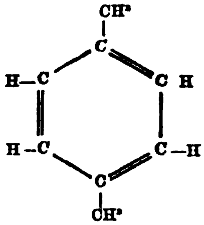
The xylidines and sulpho-acids obtained from these two nitroethylbenzenes likewise exhibit different properties. The *α-xylidine*, $C^6H^4(NH^2).C^2H^5$, is a clear liquid of sp. gr. 0·975 at 22°, boiling at 213°–214°, and quickly becoming brown in contact with the air. The *β-xylidine* has a sp. gr. of 0·975 at 22°, boils at 210°–211°, and also becomes coloured on exposure to the air. Of the aceto-xylides $C^6H^3.C^2H^4NH(C^2H^3O)$ formed by continuous boiling of these bases with acetic acid, the α modification melts at 94°, boils at 315°–317°, and is very slightly soluble in boiling water, whereas the β modification boils at 304°–305°, and dissolves very easily in boiling water.

The α and β sulpho-acids are produced by very prolonged contact of the corresponding nitroethylbenzenes with fuming sulphuric acid at 100°. The barium salt of the α sulpho-acid crystallises in broad flat needles half an inch long, containing water of crystallisation and very slightly soluble in cold water. The barium salt of the β sulpho-acid crystallises in shining silver-white anhydrous laminæ, also very slightly soluble in cold water.

Dimethyl-benzene or **Xylene.** $C^6H^4(CH^3)^2$.—The three modifications of this hydrocarbon are represented by the following formulæ:


Orthoxylene (1 : 2).


Metaxylene (1 : 3).


Paraxylene (1 : 4).

Xylene from coal-tar was formerly supposed to be identical with methyl-toluene produced synthetically by the action of sodium on a mixture of monobromotoluene and methyl iodide (v. 1056); but in 1867, Fittig, Ahrens, and Mattheides (*Ann. Ch. Pharm.* cxlvii. 15) showed that the brominated, nitrated, and amidated derivatives of methyl-toluene differ in many important particulars from those of coal-tar xylene, so that these two hydrocarbons must be regarded as isomeric, not identical. In the same year, Fittig a. Velguth (*Zeitschr. f. Chem.* [2] iii. 526), by heating mesitylenic acid, $C^9H^{10}O^2$, with lime, obtained a modification of the hydrocarbon C^8H^{10}, which they called isoxylene:

$$C^9H^{10}O^2 = C^8H^{10} + CO^2.$$

This hydrocarbon differs from methyl-toluene in not being oxidised, or but very slowly, by dilute nitric acid, and not yielding toluic acid, whereas that acid is easily obtained by oxidising methyl-toluene with nitric acid. When oxidised with chromic acid, it yields, not pulverulent terephthalic acid, but an isomeric compound, *isophthalic acid*, which crystallises in long slender needles, nearly insoluble in cold, very slightly soluble in hot water, easily soluble in alcohol. Quite recently (1869) Fittig has shown (*Zeitschr.* [2] v. 19) that coal-tar xylene is not a definite substance, but a mixture of methyl-toluene and isoxylene, the latter greatly predominating. By oxidation with potassium dichromate and sulphuric acid, Fittig obtained isophthalic acid and a small quantity of terephthalic acid, which were separated by means of boiling water, the terephthalic acid being nearly insoluble therein. Nearly half of the hydrocarbon, however, remained unattacked after 12 to 14 hours' treatment with the oxidising mixture, and this, after further oxidation for 16 hours, was for the most part converted into isophthalic acid with only a very minute quantity of terephthalic acid. The result showed that the coal-tar xylene examined contained about 90 p. c. of isoxylene, the rest consisting of methyl-toluene.

As isoxylene is formed by the decomposition of mesitylenic acid, the two methyl-atoms in its molecule have in all probability the arrangement 1 : 3, whereas in methyl-toluene, which corresponds to parachlorobenzoic acid, &c., the arrangement of the methyl-atoms is 1 : 4 (p. 199). In other words, the so-called isoxylene is a meta-compound, and is better designated as *metaxylene* or *metadimethyl-benzene*; and methyl-toluene is a para- compound, and may be called *paraxylene* or *paradimethyl-benzene*.

Now it has been shown by Fittig, Laubinger, a. Jannasch (*Zeitschr. f. Chem.* [2] iii. 577) that when an additional methyl-atom is introduced into dimethyl benzene, the compound obtained—the so-called *pseudocumene*, $C^6H^3(CH^3)^3$—is identically the same whether the dimethylbenzene used be synthetically prepared methyl-toluene, or coal-tar xylene; hence, according to the results above explained, the pseudocumene obtained will be the same, whether prepared for iso- or meta-xylene, or from para-xylene (methyl-toluene). Consequently in the trimethyl-benzene or pseudocumene obtained from either source the three methyl-atoms must exhibit the arrangement 1 : 3 : 4. Further, pseudocumene, when oxidised with dilute nitric acid, yields simultaneously two isomeric acids, *xylic* and *paraxylic*, $C^9H^{10}O^2$, which can differ from one another constitutionally only in this respect, that of the three methyl-atoms in pseudocumene, *one* has been converted into carboxyl, CO^2H, in the formation of xylic, and *another* in the formation of paraxylic acid. Pseudocumene must therefore contain two equally oxidable methyl-atoms. To determine which two out of the three possess this character, and which of the two is concerned in the formation of xylic or paraxylic acid respectively, it is necessary to remove the carboxyl groups from the two acids, and observe what modifications of dimethyl-benzene are thereby produced. Now when xylic acid prepared from synthetically formed pseudocumene is moderately heated with quicklime, it yields a distillate which, after one rectification, exhibits all the characters of pure metaxylene, boiling at 137°–138°, giving isophthalic acid by oxidation with chromic acid, and not being attacked by dilute nitric acid.

Since then in metaxylene the methyl-atoms have the places 1 : 3, it follows that in the formation of xylic acid from pseudocumene, the methyl-atom standing at the place 4 must have been oxidised to carboxyl; and from this it may be inferred that in the formation of paraxylic acid, the methyl-atom standing either at 1 or at 3 must have been oxidised to carboxyl. If in this acid the carboxyl group CO^2H stands at the place 3, its removal must yield methyl-toluene or paraxylene (1 : 4); in the contrary case a third hitherto unknown modification of dimethyl-benzene, viz. orthoxylene (1 : 2), must be formed. Now it has quite recently been shown by Bieber a. Fittig (*Zeitschr. f. Chem.* [2] v. 495) that paraxylic acid heated with quicklime yields a hydrocarbon C^8H^{10} differing both from para- and from meta-xylene. The decomposition of the paraxylic acid requires a very high temperature, but nevertheless takes place quite definitely, the hydrocarbon which distils off being obtained pure after one rectification. This hydrocarbon, orthoxylene, boils constantly at 140°–141°, that is to say, 3° higher than metaxylene, and has a peculiar odour, much less agreeable than that of meta- or of para-xylene. It is most readily distinguished from these two modifications by its behaviour with a mixture of nitric and sulphuric acids, para- and meta-xylene being easily and rapidly converted thereby at a gentle heat into well-crystallised trinitro-compounds; whereas from orthoxylene it is very difficult to obtain a solid nitro-compound (*infra*).

Dilute nitric acid slowly oxidises orthoxylene to a volatile acid, isomeric with toluic acid, which may be called *orthotoluic acid*. (See Toluic Acid.)

Xylene is produced, together with other hydrocarbons of the series, in the dry distillation of camphor (B. P. 138°–143°), and of the lime-soap of Menhaden oil (B. P. 140°–144°).

By *hydriodic acid* xylene appears to be converted into octane, C^8H^{18} (Berthelot, *Jahresb.* 1867, p. 347); by *phosphonium iodide*, PH^4I, into dimethyl-benzolin, C^8H^{14} (Baeyer, *Zeitschr.* [2] iv. 455).

In the animal organism it is converted into a peculiar modification of toluric acid (Schultzen a. Naunyn, *ibid.* 29).

Bromoxylenes.—*Dibromometaxylene*, $C^6H^2Br^2.2CH^3$, formed by treating coal-tar xylene for twenty-four hours with excess of bromine, crystallises from alcohol in nacreous laminæ, melts at 69°, boils without decomposition at 255°–256°, and does not give up any of its bromine to alcoholic potash at the boiling heat. Paradibromoparaxylene (from methyl-toluene) differs from the preceding only by its higher boiling point (72°–73°) (Fittig, Ahrens a. Mattheides, *Ann. Ch. Pharm.* cxlvii. 15; *Jahresb.* 1867, p. 697).

Chloroxylenes. See vol. v. p. 1057.

Nitroxylenes.—The properties of the nitrometa- and nitropara-xylenes, as determined by Fittig, Ahrens, a. Mattheides, agree for the most part with those previously obtained by Glinzer a. Fittig (v. 1058); but the former have further obtained two modifications of dinitroparaxylene from artificially prepared methyl-toluene [? arising from different distribution of the two atoms of NO^2).

Dinitrometaxylene (from coal-tar xylene) crystallises from alcohol in colourless, generally flattened, needles, easily soluble in hot, slightly in cold alcohol, melting at 93°.

Dinitro-paraxylene is separated by repeated crystallisation from alcohol into two modifications, α and β, the former, which is the less soluble, crystallising in very brittle needles an inch long, melting at 123·5°, the latter in rather large monoclinic crystals, melting like dinitrometaxylene at 93°.

Trinitrometaxylene, $C^8H^7(NO^2)^3$, is very easily formed by gently heating coal-tar xylene with a mixture of nitric and sulphuric acids; it is very slightly soluble in boiling, nearly insoluble in cold alcohol, and crystallises in thin, sometimes flattened needles, melting at 176°–177°. *Trinitroparaxylene*, from methyl-toluene, is much more soluble in hot alcohol, and crystallises in larger needles, melting at 137° (Fittig, Ahrens a. Mattheides). *Trinitro-orthoxylene* differs from the other two modifications in being much more difficult to crystallise. When orthoxylene is heated for an hour with the nitrating mixture, and the product poured into water, the mass which separates is almost wholly fluid, and even after six or eight hours' action, with a large excess of the acid mixture, only a semifluid mass is obtained, which gradually solidifies, and yields by solution in a little alcohol and evaporation in a vacuum, groups of small colourless crystals melting at 55°, and afterwards drops of oily liquid (Bieber a. Fittig).

Nitrobromoxylene, $C^8H^8NO^2Br$, prepared by dissolving monobromoxylene (B. P. 203°–204°) in cooled fuming nitric acid, is a slightly yellow liquid, which turns reddish on exposure to light, and boils, with partial decomposition, at 260°-265°.

Nitrodibromo-metaxylene, $C^8H^7(NO^2)Br^2$, crystallises from alcohol in long needles, melting at 108°. *Nitrobromo-paraxylene*, which is very similar to the latter, melts at about 112° (Fittig, Ahrens a. Mattheides).

AMIDOXYLENES. See XYLIDINES.

AZOXYLENE. $C^{16}H^{16}N^2$.—Produced by the action of sodium-amalgam on nitroxylene. Crystallises in brick-red needles, easily soluble in alcohol and ether; melts at 120°, and volatilises completely at higher temperatures, producing a vapour having the colour of that of bromine. Treated with excess of sodium-amalgam it is converted into a colourless body, which easily sublimes in needles; probably hydrazoxylene (Werigo, *Zeitschr. Ch. Pharm.* 1865, p. 312).

Sulpho-derivatives of Xylene.

XYLENE-SULPHUROUS ACID, $C^8H^9.SO^2H$, prepared by the action of sodium-amalgam on an ethereal solution of xylene-sulphochloride (v. 1058), is a faintly yellowish inodorous thickish oil, slightly soluble in boiling water, easily soluble in alcohol, ether, and benzol, not volatile without decomposition. It absorbs oxygen from the air, but much less quickly than benzene- or toluene-sulphurous acid, passing into xylene sulphuric acid. Its salts are not altered by oxygen. The *potassium* and *sodium salts* are easily soluble in water. The *barium salt* $(C^8H^9SO^2)^2Ba.2H^2O$ forms small white laminæ easily soluble in water, less soluble in alcohol. The *calcium salt* is similar in composition and properties. The *silver* and *lead salts* are heavy white precipitates slightly soluble in water. The *ethylic ether* $C^8H^9.SO^2C^2H^5$, obtained by boiling the acid with alcohol containing hydrochloric acid, is at ordinary temperatures an amber-yellow, scarcely fluid, nearly inodorous mass, not volatile without decomposition, insoluble in water, easily soluble in alcohol and ether.

Xylene-sulphurous acid is converted by *chlorine* into xylene-sulphochloride, $C^8H^9SO^2Cl$; by *zinc* and *sulphuric acid* into xylyl sulphydrate, $C^8H^9(SH)$; by melting *potash* into potassium sulphite and xylene; by *nitrous acid*, in alcoholic solution, into nitroxylene-sulphuric acid, and a resinous mass probably containing xylene-sulphurous ether. Heated with *water* in a sealed tube, it yields xylene-sulphuric acid and xylyl oxysulphide:

$$3C^8H^{10}SO^2 = C^8H^{10}SO^3 + C^{16}H^{18}S^2O^2 + H^2O.$$

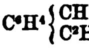
Xylyloxysulphide, $C^{16}H^{18}S^2O^2$, is a yellowish inodorous oil, insoluble in water and in aqueous alkalis, soluble in ether, alcohol, and benzol. Nascent hydrogen quickly converts it into xylene sulphydrate: $C^{16}H^{18}S^2O^2 + H^6 = 2H^2O + 2C^8H^{10}S$. Its alcoholic solution is not precipitated by silver or lead salts. With bromine it forms an uncrystallisable substitution-product, which is insoluble in water, soluble in ether and in alcohol, and dissolves partially in aqueous ammonia, forming ammonium bromide, and an amide which crystallises from the hot solution on cooling (Lindow a. Otto, *Zeitschr. f. Chem.* [2] iv. 37).

Hydrocarbons C^9H^{12}. **Cumenes.**

This molecule admits of the three metameric modifications

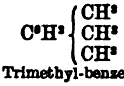
$C^6H^3(C^3H^7)$

Propyl-benzene.



$$C^6H^4\begin{cases}CH^3\\C^2H^5\end{cases}$$

Methyl-ethyl-benzene.



$$C^6H^3\begin{cases}CH^3\\CH^3\\CH^3\end{cases}$$

Trimethyl-benzene.

All three have been formed synthetically, the first by the action of sodium and propyl iodide on bromobenzene; the second by that of sodium and ethyl bromide on bromotoluene; the third by that of sodium and methyl bromide on bromotoluene.

Propyl benzene prepared as above is very much like ordinary cumene obtained by distilling cumic acid with lime, and existing ready formed in Roman cumin-oil, but boils at a temperature about 6° higher, namely at 157°, whereas ordinary cumene boils at 151°–151·5°. The synthetical compound further differs from ordinary cumene in not yielding a crystalline trinitro-derivative when treated with strong nitric and sulphuric acids, and in forming with excess of bromine a viscid tetrabrominated product, $C^9H^8O^4$, instead of the finely crystalline pentabrominated compound $C^9H^7H^5$, obtained from ordinary cumene. Both, however, when oxidised with chromic acid mixture yield the same product, namely benzoic acid. Hence it is probable that ordinary cumene likewise has the composition $C^6H^5.C^3H^7$, but that it consists of *isopropyl-benzene*, $C^6H^5.CH(CH^3)^2$, whereas the product obtained by the action of sodium and propyl iodide consists of *normal propyl-benzene*, $C^6H^5.CH^2CH^2CH^3$. This supposition is in accordance with the lower boiling point of ordinary cumene, as it is a general rule that isopropyl-compounds boil at lower temperatures than the corresponding normal propyl-compounds. It has not, however, been found possible to verify this conclusion by the synthetical preparation of isopropyl-benzene, isopropyl iodide not being attacked by sodium even when heated with it in sealed tubes (Fittig, Schäffer a. König, *Ann. Ch. Pharm.* cxlix. 324).

The compounds $C^6H^4(CH^3)(C^2H^5)$ and $C^6H^3(CH^3)^3$ each admit of three isomeric modifications, those of the former being denoted by the formulæ 1 : 2, 1 : 3, 1 : 4; those of the latter by 1 : 2 : 3, 1 : 2 : 4, and 1 : 3 : 5. Of ethyl-methyl-benzene, however, only one modification is actually known; but of trimethyl-benzene two have been distinguished with certainty, and the third appears also to occur in coal-naphtha.

Fittig has shown that the trimethyl-benzenes, or pseudocumenes, produced synthetically by the introduction of an atom of methyl into metaxylene and paraxylene (p. 293), are identical, both boiling at 166° and exhibiting exactly the same behaviour with various agents, yielding, for example, the same highly characteristic bromo- and nitro-substitution-products, and the same oxidation-products, viz. two isomeric monobasic acids, xylic and paraxylic, and one bibasic acid, xylidic acid. The identity of the two trimethyl-benzenes thus produced is easily explained, if we suppose that when an atom of bromine is introduced into metaxylene and paraxylene respectively, it takes the place of a hydrogen-atom which, in the isomeric compound, is replaced by methyl: thus the compounds

$$\underset{\text{Bromometaxylene}}{C^6MeHMeBrHH} \quad \text{and} \quad \underset{\text{Bromoparaxylene}}{C^6MeHBrMeHH}$$

must evidently, when the bromine in each is replaced by methyl, yield the same trimethyl-benzene, 1 : 3 : 4 or $C^6MeHMeMeHH$.

The 9-carbon homologue of benzene, boiling at about 164°–167°, obtained from coal-naphtha, is generally regarded as a definite modification of trimethyl-benzene and designated as pseudocumene. But the recent experiments of Fittig a. Wackenroder have shown that this portion of coal-naphtha contains in all cases two, and sometimes three modifications of trimethyl-benzene, one of which, often greatly predominating, is mesitylene; the second identical with the synthetically formed compound just mentioned; while the third is a modification not hitherto observed. These three modifications are separated by treatment with a mixture of nitric and sulphuric acid, whereby they are converted into trinitro-compounds, $C^9H^9(NO^2)^3$, easily separable by solution in hot benzol, the trinitromesitylene, melting at 232°, separating out first; then the trinitro-pseudocumene, melting at 185° (identical with that obtained from synthetically prepared pseudocumene); and lastly the trinitro compound of the third modification above mentioned, which melts at a lower temperature. The relative positions of the three methyl-atoms in the three modifications have not yet been determined. The hydrocarbon boiling between 164° and 167° obtained by distilling camphor with zinc chloride appears also to consist mainly of mesitylene (Fittig, *Zeitschr. f. Chem.* [2] iv. 577–584).

Pseudocumene (from coal-tar) is almost completely decomposed when its vapour is passed through a red-hot tube, yielding benzene, toluene, xylene, naphthalene, and a naphthalene hydride boiling at 200°, together with smaller quantities of liquid hydrocarbons boiling between 250° and 320°; also anthracene and chrysene, and a gaseous mixture of hydrogen and marsh-gas, with a small quantity of ethylene and a trace of acetylene. The formation of naphthalene appears to be correlative with that of the lower homologues of cumene; thus:

$$\underset{\text{Cumene.}}{2C^9H^{12}} = \underset{\text{Naphthalene.}}{C^{10}H^8} + \underset{\text{Xylene.}}{C^8H^{10}} \quad 3H^2.$$

(Berthelot, *Bull. Soc. Chim.* [2] vii. 229; *Jahresb.* 1866, p. 543.)

Pseudocumene heated with 80 pts. of strong *hydriodic acid* is converted into nonane, C^9H^{20}, with separation of a large quantity of iodine; with 20 pts. of the acid, the products are propane and free carbon:

$$C^9H^{12} + 6HI = 2C^3H^8 + C^3 + H^2 + 3I^2$$

(Berthelot, *Bull. Soc. Chim.* [2] vii. 53; *Jahresb.* 1867, p. 346).

Pseudocumene (obtained from coal-tar and by synthesis) yields by oxidation with *chromic acid* the two isomeric acids xylie and paraxylic, $C^9H^{10}O^2$; according to Beilstein (*Zeitschr.* [2] iv. 672), coal-tar cumene also yields another acid isomeric with these, viz. mesitylenic acid.

Propyl-benzene, from Roman cumin-oil, is converted by bromine in contact with water into dibromobenzoic acid (Meusel, *Jahresb.* 1867, p. 698).

BROMOCUMENES.—*Monobromocumene*, $C^6H^4Br.C^3H^7$, formed when bromine is left in contact with cumene from Roman cumin-oil, boils after repeated rectification at 218°–220°, and has a sp. gr. of 1·3223 at 13°. It is not attacked by alcoholic potash, and when oxidised with potassium dichromate and sulphuric acid yields parabromobenzoic (bromodracylic) acid and acetic acid. The same hydrocarbon treated for a considerable time with excess of bromine forms the compound $C^9H^7Br^5$, or probably $C^6Br^5.C^3H^7$, which crystallises from warm alcohol in concentric groups of prisms melting at 90°–100°, and decomposing at a higher temperature (E. Meusel, *Zeitschr. f. Chem.* [2] iii. 322; *Jahresb.* 1867, p. 698). Synthetically prepared propyl benzene forms with excess of bromine a viscid uncrystallisable product, $C^9H^8H^4$ (p. 294).

Pseudocumene gently treated with 6 at. bromine forms the *tribrominated* compound $C^9H^9Br^3$, which crystallises in a freezing mixture. With 4 at. bromine, a *dibrominated* compound appears to be formed, since it is converted by fuming nitric acid into $C^9H^8(NO^2)^2Br^2$ (Riche a. Bérard, *Bull. Soc. Chim.* [2] ii. 305).

When bromine is dropped into cooled pseudocumene, prepared synthetically from bromometaxylene, the whole quickly solidifies to *monobromopseudocumene*, $C^6H^2Br.(CH^3)^3$; but on adding more bromine, the whole again becomes liquid, and is converted into *tribromopseudocumene*, $C^9H^9Br^3$, or probably $C^6Br^3.(CH^3)^3$, which dissolves very sparingly in boiling alcohol, and crystallises therefrom in capillary needles an inch long, melting at 225°, and resembling tribromomesitylene in every respect, excepting that they are flexible, whereas the crystals of tribromomesitylene are brittle and easily crumbled to powder (Fittig a. Laubinger, *Zeitschr. f. Chem.* [2] iv. 578).

NITROCUMENES.—*Mononitropseudocumene* is formed when pseudocumene (prepared from bromometaxylene) is dropped into cold fuming nitric acid; also as a bye-product in the oxidation of pseudocumene by dilute nitric acid. It crystallises from alcohol in long colourless needles, melting at 71°, and boiling without decomposition at 265°. By reduction with *tin* and *hydrochloric acid* it yields the double salt of cumidine hydrochloride and stannous chloride, $C^9H^{11}(NH^2).HCl.SnCl^2$. By oxidation with *chromic acid*, it is converted into paranitroxylic acid, $C^8H^7(NO^2)O^2$ (Schaper, *Zeitschr. f. Chem.* [2] iii. 12; Fittig a. Laubinger, *ibid.* iv. 577). Ammonium sulphite converts nitrocumene into *disulphuryl-cumenylic acid*, $C^9H^{13}NS^2O^6$ (Carius, *Jahresb.* 1861, p. 635).

Dinitropseudocumene was not obtained by Fittig a. Laubinger in the pure state, but it appears to be fluid at ordinary temperatures.

Trinitropseudocumene, $C^9H^9(NO^2)^3$, is obtained by dropping the hydrocarbon into a cooled mixture of fuming nitric and sulphuric acids, and separates immediately as a crystalline mass. It is very slightly soluble in boiling alcohol, more soluble in benzol, and crystallises from alcohol by slow cooling in stellate groups of colourless needles; from benzol in short compact hard prisms mostly flattened. It melts at 185° and sublimes at a stronger heat. Treated in alcoholic ammoniacal solution with hydrogen sulphide, it is at first converted into a compound very much like dinitro-amidomesitylene, but much less stable, which is dissolved by strong hydrochloric acid, but precipitated therefrom by water. By prolonged treatment with the reducing agent, there is formed a well-marked very stable base, crystallising from water and alcohol in golden-yellow prisms, melting at 137°, but consisting, not, as might be supposed, of diamido-nitropseudocumene, $C^9H^9(NH^2)^2NO^2$, but of *amidonitropseudocumene*, $C^9H^{10}(NH^2)NO^2$. The diamidonitro-compound is doubtless formed in the first instance, but afterwards loses an atom of NH^2 by inverse substitution. *Amidonitropseudocumene* is distinguished by the sparing solubility and great crystallising tendency of its salts, especially the *sulphate*, $[C^9H^{10}(NH^2)NO^2]^2H^2SO^4.H^2O$, which is quite insoluble in cold water, and crystallises from boiling water in extremely thin, perfectly transparent and colourless quadratic tables (Fittig a. Laubinger).

Trinitropseudocumene is also formed by the action of the nitro-sulphuric acid mixture on the cumene of coal-tar, but not nearly in so large a quantity as the isomeric compound trinitro-mesitylene (p. 299).

PSEUDOCUMENE-SULPHURIC ACID, $C^9H^{11}SO^3H$, is obtained by the action of a mixture of ordinary and fuming sulphuric acid on rectified coal-tar cumene. The solution diluted with water and neutralised with barium carbonate, yields *barium pseudocumene-sulphate*, $(C^9H^{11}SO^3)^2Ba.2H^2O$, as a white, fine-grained powder, which is but slightly soluble in water, and gives off its water of crystallisation above 170°. The *lead*, *copper*, and *calcium* salts are very soluble in water. The acid separated from the barium salt is resolved by heating its concentrated solution in the oil-bath into sulphuric acid and pseudocumene boiling at 166°.

Fuming sulphuric acid alone acts with great violence on pseudocumene, forming a smaller quantity of pseudocumene-sulphuric acid; and on diluting with water, a solid body separates, insoluble in water, alcohol, ether, and benzene, and probably consisting of sulphocumide, $(C^9H^{11})^2SO^2$.

Pseudocumene-sulphochloride, $C^9H^{11}SO^2Cl$, which separates as an oil on triturating sodium pseudocumene-sulphate with phosphorus pentachloride, and adding water, is converted by the action of zinc and sulphuric acid into a solid, inodorous body having the composition of cumyl sulphydrate, $C^9H^{11}SH$; it crystallises from alcohol in nacreous laminæ, melting at 86°–87° and boiling at about 235° (Beilstein a. Kögler, *Ann. Ch. Pharm.* cxxxvii. 117; *Jahresb.* 1865, p. 559).

Mesitylene. $C^6H^3(CH^3)^3$.—This hydrocarbon, originally obtained by the action of sulphuric acid upon acetone, has been shown by Fittig a. Wackenroder to constitute the chief portion of the fraction of coal-naphtha which boils at 164°–167°, also of that portion of the distillate obtained by heating camphor with zinc chloride which boils at the same temperature. This being the case, it is evident that many of the supposed derivatives of pseudocumene obtained by former experimenters were not pure products, but consisted to a great extent of derivatives of mesitylene, the latter sometimes greatly predominating. Even the purified pseudocumene which Beilstein a. Kögler obtained by distilling the sulpho-acid prepared from coal-tar cumene (p. 297) has been shown by Fittig a. Wackenroder to consist of mesitylene. On the other hand, the great similarity between pseudocumene and mesitylene, as exhibited especially in their tribromo- and trinitro- derivatives, while it shows that mesitylene is in all probability an isomeric variety of trimethyl-benzene, renders it a matter of great difficulty to separate mesitylene from pseudocumene in mixtures of the two, such as coal-tar cumene. Hence to obtain pure mesitylene we must still resort to Kane's mode of preparation from acetone.

Fittig a. Brückner (*Ann. Ch. Pharm.* cxlvii. 42) prepare mesitylene as follows: 1 vol. commercial acetone is introduced into a large tubulated retort containing dry sand; a cooled mixture of 1 vol. sulphuric acid and ½ vol. water is added in a slow but continuous stream; and the mixture, after standing for 24 hours, is distilled, the receiver being changed as soon as oily streaks appear in the neck of the retort. There then passes over, together with the watery vapours, an oil, chiefly consisting of mesitylene, after which sulphurous anhydride is evolved, and the contents of the retort acquire a transient but deep indigo-blue colour. The oily distillate washed with water and soda-ley yields by fractional distillation, finally over sodium, pure mesitylene boiling constantly at 163°. The higher portion of the crude mesitylene, passing over up to 300°, contains a hydrocarbon boiling at 194°–196°, probably $C^{10}H^{14}$.

Mesitylene boiled for 16 to 20 hours with *dilute nitric acid*, is oxidised to mesitylenic acid, $C^9H^{10}O^2$, isomeric with xylic acid (Fittig, *Jahresb.* 1866, p. 610). With *potassium dichromate* and *sulphuric acid* it yields a large quantity of acetic acid, and by complete oxidation also a small quantity of an acid which is sparingly soluble in cold water, sublimable, crystallises in prisms, and forms a barium salt crystallising from hot water in long needles (Fittig, *Jahresb.* 1865, p. 560). By *phosphonium iodide* at 280°, it is converted into a hydrocarbon, C^9H^{18}, boiling at 138° (Baeyer, *Zeitschr. f. Chem.* [2] v. 320).

Bromomesitylenes.—*Monobromomesitylene*, $C^9H^{11}Br$, produced by carefully mixing well-cooled mesitylene with 2 at. bromine, and purified in the usual way, is a limpid oil, having an aromatic odour, a sp. gr. of 1·3191 at 10°, boiling at 225°, solidifying completely in a freezing mixture, and melting again at + 1°; not attacked by sodium-amalgam at any temperature. *Di-* and *tri-bromomesitylene* are contained in the residue left after distilling off the monobrominated compound obtained as above, and are produced in larger quantity by the action of 4 at. bromine on mesitylene. On recrystallising from alcohol, the tribrominated compound separates out almost completely, while dibromomesitylene, $C^9H^{10}Br^2$, remains in the mother-liquor, and may be crystallised therefrom in colourless needles an inch long, melting at 60°, and distilling without decomposition at 285°. *Tribromomesitylene*, $C^9H^9Br^3$, previously obtained by Hofmann and Cahours (iii. 930), is nearly insoluble in cold alcohol, and crystallises from benzol by spontaneous evaporation in transparent monoclinic prisms melting at 224° (Fittig a. Storer, *Ann. Ch. Pharm.* cxlvii. 1; *Jahresb.* 1867, p. 703).

Chloromesitylenes (Fittig a. Hoogewerff, *Zeitschr. f. Chem.* [2] v. 168).—Chlorine acts very strongly on mesitylene, even in the cold, the three hydrogen-atoms in the benzene residue, C^6H^3, being easily replaced by chlorine. The di- and trichlorinated compounds are indeed always produced, together with monochloromesitylene, even when the quantity of chlorine passed into the liquid is less than sufficient for the complete conversion of the mesitylene into the latter. To separate the three at 218°–220°, and has a sp. gr. of 1·3223 at 13°. It is not attacked by alcoholic potash, and when oxidised with potassium dichromate and sulphuric acid yields parabromobenzoic (bromodracylic) acid and acetic acid. The same hydrocarbon treated for a considerable time with excess of bromine forms the compound $C^9H^7Br^5$, or probably $C^6Br^5.C^3H^7$, which crystallises from warm alcohol in concentric groups of prisms melting at 90°–100°, and decomposing at a higher temperature (E. Meusel, *Zeitschr. f. Chem.* [2] iii. 322; *Jahresb.* 1867, p. 698). Synthetically prepared propyl benzene forms with excess of bromine a viscid uncrystallisable product, $C^9H^8H^4$ (p. 294).

Pseudocumene gently treated with 6 at. bromine forms the *tribrominated* compound $C^9H^9Br^3$, which crystallises in a freezing mixture. With 4 at. bromine, a *dibrominated* compound appears to be formed, since it is converted by fuming nitric acid into $C^9H^8(NO^2)^2Br^2$ (Riche a. Bérard, *Bull. Soc. Chim.* [2] ii. 305).

When bromine is dropped into cooled pseudocumene, prepared synthetically from bromometaxylene, the whole quickly solidifies to *monobromopseudocumene*, $C^6H^2Br.(CH^3)^3$; but on adding more bromine, the whole again becomes liquid, and is converted into *tribromopseudocumene*, $C^9H^9Br^3$, or probably $C^6Br^3.(CH^3)^3$, which dissolves very sparingly in boiling alcohol, and crystallises therefrom in capillary needles an inch long, melting at 225°, and resembling tribromomesitylene in every respect, excepting that they are flexible, whereas the crystals of tribromomesitylene are brittle and easily crumbled to powder (Fittig a. Laubinger, *Zeitschr. f. Chem.* [2] iv. 578).

NITROCUMENES.—*Mononitropseudocumene* is formed when pseudocumene (prepared from bromometaxylene) is dropped into cold fuming nitric acid; also as a bye-product in the oxidation of pseudocumene by dilute nitric acid. It crystallises from alcohol in long colourless needles, melting at 71°, and boiling without decomposition at 265°. By reduction with *tin* and *hydrochloric acid* it yields the double salt of cumidine hydrochloride and stannous chloride, $C^9H^{11}(NH^2).HCl.SnCl^2$. By oxidation with *chromic acid*, it is converted into paranitroxylic acid, $C^9H^9(NO^2)O^2$ (Schaper, *Zeitschr. f. Chem.* [2] iii. 12; Fittig a. Laubinger, *ibid.* iv. 577). Ammonium sulphite converts nitrocumene into *disulphuryl-cumenylic acid*, $C^9H^{13}NS^2O^6$ (Carius, *Jahresb.* 1861, p. 635).

Dinitropseudocumene was not obtained by Fittig a. Laubinger in the pure state, but it appears to be fluid at ordinary temperatures.

Trinitropseudocumene, $C^9H^9(NO^2)^3$, is obtained by dropping the hydrocarbon into a cooled mixture of fuming nitric and sulphuric acids, and separates immediately as a crystalline mass. It is very slightly soluble in boiling alcohol, more soluble in benzol, and crystallises from alcohol by slow cooling in stellate groups of colourless needles; from benzol in short compact hard prisms mostly flattened. It melts at 185° and sublimes at a stronger heat. Treated in alcoholic ammoniacal solution with hydrogen sulphide, it is at first converted into a compound very much like dinitro-amidomesitylene, but much less stable, which is dissolved by strong hydrochloric acid, but precipitated therefrom by water. By prolonged treatment with the reducing agent, there is formed a well-marked very stable base, crystallising from water and alcohol in golden-yellow prisms, melting at 137°, but consisting, not, as might be supposed, of diamido-nitropseudocumene, $C^9H^9(NH^2)^2NO^2$, but of *amidonitropseudocumene*, $C^9H^{10}(NH^2)NO^2$. The diamidonitro-compound is doubtless formed in the first instance, but afterwards loses an atom of NH^3 by inverse substitution. *Amidonitropseudocumene* is distinguished by the sparing solubility and great crystallising tendency of its salts, especially the *sulphate*, $[C^9H^{10}(NH^2)NO^2]^2H^2SO^4.H^2O$, which is quite insoluble in cold water, and crystallises from boiling water in extremely thin, perfectly transparent and colourless quadratic tables (Fittig a. Laubinger).

Trinitropseudocumene is also formed by the action of the nitro-sulphuric acid mixture on the cumene of coal-tar, but not nearly in so large a quantity as the isomeric compound trinitro-mesitylene (p. 299).

PSEUDOCUMENE-SULPHURIC ACID, $C^9H^{11}SO^3H$, is obtained by the action of a mixture of ordinary and fuming sulphuric acid on rectified coal-tar cumene. The solution diluted with water and neutralised with barium carbonate, yields *barium pseudocumene-sulphate*, $(C^9H^{11}SO^3)^2Ba.2H^2O$, as a white, fine-grained powder, which is but slightly soluble in water, and gives off its water of crystallisation above 170°. The *lead*, *copper*, and *calcium* salts are very soluble in water. The acid separated from the barium salt is resolved by heating its concentrated solution in the oil-bath into sulphuric acid and pseudocumene boiling at 166°.

Fuming sulphuric acid alone acts with great violence on pseudocumene, forming a smaller quantity of pseudocumene-sulphuric acid; and on diluting with water, a solid

AMIDOMESITYLENE OF MESIDINE. $C^9H^{11}(NH^2) = C^6H^2(NH^2).(CH^3)^3$ (Fittig a. Storer, *Ann. Ch. Pharm.* cxlvii. 1).—Produced by boiling nitromesitylene with tin and hydrochloric acid, and separated from the hydrochloride by ammonia in colourless oil-drops which do not solidify at 0°. The *hydrochloride*, $C^9H^{11}(NH^2).HCl$, forms feathery crystals or large transparent prisms easily soluble in water and in alcohol. The *stannoso-chloride*, $2(C^9H^{13}N.HCl).SnCl^2$, forms needle-shaped, rather sparingly soluble crystals, which are decomposed by pure water. The *oxalate*, $(C^9H^{13}N)^2.C^2H^2O^4$, is a precipitate, consisting of crystalline laminæ, sparingly soluble in cold water, and dissolving with decomposition in boiling water, so that the salt cannot be recovered from the solution.

Dinitro-amidomesitylene or *Dinitromesidine*, $C^9H^9(NO^2)^2.NH^2$, is formed, together with nitro-diamidomesitylene, by prolonged treatment of trinitromesitylene with ammonium sulphide. From the evaporated residue the latter base is extracted by dilute hydrochloric acid, and the undissolved portion treated with more concentrated acid yields the dinitro-amidomesitylene, which may be purified by precipitation with water and recrystallisation from alcohol. It is insoluble in water, but dissolves easily in hot alcohol, and crystallises therefrom in sulphur-yellow, very well defined short prisms, melting at 193°–194°, and volatilising without decomposition. The only acid with which it appears to unite is concentrated hydrochloric acid, and even the compound thus formed is easily decomposed by water (Fittig).

DIAMIDOMESITYLENE or **MESITYLENE-DIAMINE**, $C^9H^{10}(NH^2)^2$, is produced by heating dinitromesitylene with tin and concentrated hydrochloric acid, precipitating the tin by hydrogen sulphide, evaporating the filtrate to dryness, recrystallising the salt from moderately strong hydrochloric acid, and precipitating with ammonia. It then separates as a nearly colourless oil, which gradually solidifies to a pulp of long slender crystals. It dissolves easily in hot water, alcohol, or ether, and crystallises from water in long capillary needles, from ether in large monoclinic crystals; becomes yellow or reddish on exposure to light; melts at 90°, and sublimes in needles without decomposition. Bromine water added to the aqueous solution throws down a liquid compound insoluble in hydrochloric acid. The *hydrochloride*, $C^9H^{14}N^2.2HCl$, crystallises in square tables, easily soluble in water and in alcohol, and is precipitated almost completely from the aqueous solution by hydrochloric acid of a certain strength; does not form a double salt with platinic chloride. The *nitrate* is very soluble and crystallisable. The *oxalate*, $C^9H^{14}N^2.C^2H^2O^4$, is sparingly soluble in alcohol, and crystallises from hot water in hard grains. The *sulphate*, $C^9H^4N^2.SH^2O^4$, is very soluble in water, scarcely at all in cold alcohol, and crystallises from alcohol in broad transparent laminæ, which quickly become dull when exposed to the air (Fittig).

Nitro-diamidomesitylene or *Nitromesitylene-diamine*, $C^9H^9(NO^2)(NH^2)^2$, is formed, as already observed, simultaneously with dinitro-amidomesitylene, by the action of ammonium sulphide on trinitromositylene, and is extracted from the evaporated residue by dilute hydrochloric acid. From this solution it is separated by ammonia, as a deep yellow amorphous precipitate, which dissolves but sparingly in hot water, easily in alcohol and ether. From water it crystallises in large orange-coloured laminæ; from alcohol, by spontaneous evaporation, in very large well-defined monoclinic prisms having a very brilliant lustre and nearly the colour of sodium nitroprusside. They exhibit the combination $\infty P.[\grave{P}\infty].oP$, and are shortened in the direction of the principal axis. Angle $\infty P : \infty P$, in the orthodiagonal principal section, $= 113° 14'$; $\infty P : oP = 101° 20'$; $[P\infty] : oP = 158° 44'$; $[P\infty] : [\grave{P}\infty]$ at the principal axis $= 137° 28'$; acute angle of axes $= 60° 4'$. Ratio of clinodiagonal, orthodiagonal, and principal axis $= 1{\cdot}6248 : 1 : 0{\cdot}4167$. Melting point 184°. The *hydrochloride*, $C^9H^9NO^2(NH^2)^2.2HCl$, dissolves easily in water and in alcohol, and crystallises in colourless square tables (Fittig).

Sulpho-derivatives of Mesitylene.

MESITYLENE-SULPHURIC or **SULPHOMESITYLIC ACID**, $C^9H^{11}.SO^3H$, is formed by dissolving mesitylene in warmed fuming sulphuric acid, and separates for the most part in needles as the solution cools. The pure acid separated from the barium salt forms, when evaporated over oil of vitriol, a syrup which soon solidifies to a colourless radio-crystalline mass. The *barium salt* $(C^9H^{11}SO^3)^2Ba$ crystallises from hot water in colourless laminæ. The *potassium salt* $C^9H^{11}SO^3K$ is very soluble in water, and crystallises from alcohol in small laminæ, united in spherical groups (Fittig, *Jahresb.* 1866, p. 610). The *silver* and *lead* salts were examined by Hofmann (iii. 931).

The sulpho-acid which Beilstein and Kögler obtained (*Ann. Ch. Pharm.* cxxxvii.

chlorinated compounds, the mixture is washed with soda-ley and dissolved in boiling alcohol. The solution on cooling deposits nearly the whole of the trichloromesitylene, which is easily obtained quite pure by recrystallisation from alcohol. The mono- and dichlorinated compounds may be separated from the mother-liquor by evaporating off the alcohol and subjecting the remaining liquid to fractional distillation. When monochloromesitylene is the only product sought, it is best to treat the mesitylene with only half the required quantity of chlorine, and immediately subject the liquid to fractional distillation.

Monochloromesitylene, $C^6H^2Cl.(CH^3)^3$, is a transparent colourless liquid, very soluble in alcohol, and boiling without decomposition at 204°–206°. It is slowly oxidised by a mixture of *potassium dichromate* and *sulphuric acid*, yielding acetic acid, together with other products. By *dilute nitric acid* it is easily oxidised to chloromesitylenic acid. *Fuming nitric acid* attacks it very strongly, even when well cooled, converting it instantly into a mixture of mono- and dinitro-chloromesitylene. *Mononitrochlorcmesitylene*, $C^6H(NO^2)Cl.(CH^3)^3$, is found, in small quantity only, in the reaction just mentioned; also as a bye-product in the oxidation of chloromesitylene by dilute nitric acid. It forms groups of spicular crystals melting at 56°–57°, easily soluble in alcohol. *Dinitrochloromesitylene*, $C^6(NO^2)^2Cl.(CH^3)^3$, the chief product of the action of fuming nitric acid on chloromesitylene, crystallises from alcohol in long colourless needles, which melt at 176°–177°, may be sublimed without decomposition, dissolve easily in hot, sparingly in cold alcohol.

Dichloromesitylene, $C^6HCl^2.(CH^3)^3$, crystallises from alcohol in splendid colourless shining prisms, melting at 59°, boiling without decomposition at 243°–244°, very soluble in hot alcohol, also in ether and in benzol. Scarcely attacked by chromic acid mixture, even after several days' boiling, yielding a barely perceptible quantity of acetic acid and not a trace of any aromatic acid.

Trichloromesitylene. $C^6Cl^3.(CH^3)^3$.—This compound, first prepared by Kane (iii. 930), is the only product formed when mesitylene is treated at ordinary temperatures with excess of chlorine. It is very slightly soluble in cold alcohol, somewhat more in hot alcohol, easily in ether. From boiling alcohol it crystallises in long, slender, colourless needles, melting at 204°–205°, and subliming without decomposition in long brilliant spiculæ. It does not suffer the least alteration by boiling for several days with nitric acid, chromic acid, or potassium permanganate (Fittig a. Hoogewerff).

HYDROXYL-MESITYLENE. See MESITYLENOL.

NITROMESITYLENES.—***Mononitromesitylene***, $C^6H^2(NO^2).(CH^3)^3$, is formed on warming mesitylene with nitric acid of sp. gr. 1·38; also as a bye-product in the preparation of mesitylenic acid; it is purified by distillation with aqueous vapour, rectification *per se*, and crystallisation of the solidifying portion from alcohol. Crystallises in well-defined transparent prisms an inch long, or in large tabular crystals; dissolves in almost all proportions of boiling alcohol, melts at 41°, and boils without decomposition at 240°-250°. It is not converted into nitromesitylenic acid by boiling with potassium dichromate and dilute sulphuric acid. *Nitrobromomesitylene*, $C^9H^{10}(NO^2)Br$, formed, together with a small quantity of the following compound, by leaving bromomesitylene in contact with a mixture of equal volumes of fuming and ordinary nitric acid at ordinary temperatures, is moderately soluble in alcohol, and separates therefrom by spontaneous evaporation in colourless crystals, very much like those of sal-ammoniac, crystallised from water; they melt at 54°. *Dinitrobromomesitylene*, $C^9H^9(NO^2)^2Br$, formed at ordinary temperatures by drenching bromomesitylene with fuming nitric acid, dissolves slightly in cold, more freely in boiling alcohol, crystallises in colourless needles, and melts at 189°–190°, emitting a musk-like odour (Fittig a. Störer).

Dinitromesitylene, $C^9H^{10}(NO^2)^2$, is easily formed by dropping mesitylene into cooled fuming nitric acid; melts at 86°; dissolves with moderate facility in hot, less easily in cold alcohol; and crystallises in colourless rhombic prisms an inch long, exhibiting the combination $\infty P\ .\ \infty\breve{P}\infty\ .\ oP$, the ratio of the macrodiagonal to the brachydiagonal being 1 : 0·5475; angle $\infty P : \infty\breve{P}\infty = 118° 52'$.

Trinitromesitylene, $C^9H^9(NO^2)^3$, obtained by dropping mesitylene into a mixture of 1 vol. fuming nitric and 2 vol. strong sulphuric acid, is nearly insoluble in cold, very sparingly soluble in boiling alcohol, and crystallises therefrom in slender colourless needles; from acetone in large prisms having a glassy lustre; melts at 230°–232° (Fittig, *Ann. Ch. Pharm.* cxli. 129). The preparation of this compound from the mixture of hydrocarbons constituting coal-tar cumene has already been noticed (p. 296).

Dilute nitric acid, on the other hand, oxidises only one of the ethyl-atoms, producing ethyl-benzoic acid, isomeric with xylic acid:

$$C^6H^4\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right. + O^6 = C^6H^4\left\{\begin{matrix}CO^2H\\C^2H^5\end{matrix}\right. + CO^2 + 2H^2O.$$

By further oxidation, however, with stronger nitric acid, the ethyl-benzoic acid is converted into terephthalic acid (Fittig a. König, *Ann. Ch. Pharm.* cxliv. 277).

Diethyl-benzene dissolves in fuming sulphuric acid, forming diethylbenzene-sulphuric acid, $C^6H^3(C^2H^5)^2.SO^3H$, which crystallises in deliquescent laminæ. Its *barium salt*, $(C^{10}H^{13}SO^3)^2Ba$, crystallises from alcohol in nodules or laminæ; the *potassium salt* $C^{10}H^{13}SO^3K$ in slender needles (Fittig a. König).

Ethyl-dimethyl-benzene or **Ethyl-xylene,** $C^6H^3(CH^3)^2C^2H^5$, has a sp. gr. of 0·8783 at 30° and boils at 183°–184°. By warming with a mixture of nitric and sulphuric acids, it is converted into a trinitro-compound which crystallises from alcohol in needles melting at 119°. By oxidation with chromic acid, it yields, together with acetic acid, an acid similar to terephthalic acid, but more soluble in alcohol (Fittig a. Ernst, *Zeitschr. f. Chem.* [2] i. 572).

Cymene. There are two metameric hydrocarbons to which this name is applied: α cymene, obtained from Roman cumin-oil and from the oil of water-hemlock seed, in which it exists ready-formed; also produced, together with several of its homologues, by the dehydration of common camphor with fused zinc chloride, phosphoric oxide, P^2O^5, or phosphoric sulphide, P^2S^5; and β cymene which occurs amongst the products of the destructive distillation of coal.

α *Cymene.*—The preparation of this modification from Roman cumin-oil and from the oil of *Cicuta virosa* is described in vol. ii. p. 296. The portion of the distillate obtained by treating camphor with fused zinc-chloride, which passes over between 173° and 176°, consists mainly of α cymene (Fittig, Köbrich a. Jilke, *Jahresb.* 1867, p. 701); and by distilling camphor with phosphoric sulphide, cymene is obtained without any admixture of other hydrocarbons:

$$5C^{10}H^{16}O + P^2S^5 = 5C^{10}H^{14} + P^2O^5 + 5H^2S.$$

This is therefore the best method of obtaining cymene from camphor: On mixing 1 mol. phosphoric sulphide in a capacious retort with 5 mol. coarsely comminuted camphor, and applying a gentle heat, the mass fuses to a brown liquid, which, when more strongly heated, yields a large quantity of cymene, to be purified by agitation with strong potash-ley, then with water, and drying over calcium chloride (R. Pott, *Zeitschr. f. Chem.* [2] v. 200). The same modification of cymene appears to be obtained by the distillation of cumin-oil with phosphoric oxide (Louguinine, *Jahresb.* 1867, p. 692), and of carvol (from cumin-oil) with zinc-powder (a mixture of metallic zinc, zinc oxide, and hydrate) (Arndt, *Zeitschr.* [2] iv. 730).

α Cymene from camphor boils at 175°–178° (Pott); at 177°–179° (Louguinine, p. 278); that from Roman cumin-oil at 177·5° (Kopp); at 179·5° (corr.) (Warren, *Jahresb.* 1865, p. 515); at 175°–176° (Louguinine). Sp. gr. of that from camphor 0·8768 and 0·8732 at 0° (Louguinine); sp. gr. of that from cumin-oil 0·8705 at 0° (Louguinine); 0·8660 at 15° (Mendelejef, *Jahresb.* 1863, p. 7). Cymene from either source is converted by oxidation with dilute nitric acid into toluic acid, $C^6H^4\left\{\begin{matrix}CH^3\\CO^2H\end{matrix}\right.$; by further oxidation with chromic acid mixture, into acetic acid and terephthalic acid, $C^6H^4.(CO^2H)^2$. Consequently α cymene contains two lateral chains (p. 200), one of which is methyl; that is to say, it has the constitution of propyl-methyl-benzene, $C^6H^4\left\{\begin{matrix}C^3H^7\\CH^3\end{matrix}\right.$.

Propyl-methyl-benzene prepared by the action of sodium and propyl-iodide on bromotoluene boils at nearly the same temperature as α cymene (178°-179°); is also converted by oxidation into toluic and afterwards into terephthalic acid; yields a sulpho-acid whose barium salt agrees in crystalline form and amount of water with that of α cymene-sulphuric acid, and indeed appears to resemble α cymene in every respect excepting that its nitro-derivatives do not crystallise. From the analogy of cumene (p. 295), it is probable that the synthetically prepared compound may be normal propyl-toluene, and that α cymene may be isopropyl-toluene (Fittig, Schäffer a. König, *Ann. Ch. Pharm.* cxlix. 337).

α Cymene (from camphor) is converted by fuming sulphuric acid into cymene-sulphuric acid, $C^{10}H^{13}SO^3H$, the barium salt of which, $(C^{10}H^{13}SO^3)^2Ba.6H^2O$, crystallises in easily soluble rhombic prisms (Fittig, Köbrich a. Jilke; Pott). When the potassium salt of this acid is fused with 2 pts. potassium hydrate, the fused mass dissolved in water, the solution acidulated with sulphuric acid, and the separated brown oil distilled, a yellowish viscid oil is obtained boiling at 230° and having the composition of cymic phenol, $C^{10}H^{14}O$, isomeric with thymol. It is distinguished from the latter by not solidifying in a freezing mixture, and by being but slowly converted into a sulpho-acid, $C^{10}H^{13}O.SO^3H$, by the action of fuming sulphuric acid (Pott).

According to Riche a. Bérard (*Bull. Soc. Chim.* [2] ii. 205), cymene from camphor left in contact with 4 at. bromine, forms crystallisable *dibromocymene*, $C^{10}H^{12}Br^2$, but that obtained from Roman cumin-oil does not yield this compound [?]; with an excess of bromine however it forms a small quantity of a more highly brominated crystalline compound. *Nitrocymene* (prepared from the cymene of Roman cumin-oil) is converted by sodium-amalgam into azocymene, $C^{20}H^{26}N^2$ (Werigo).

β Cymene is contained in coal-tar, chiefly in the heavy oil boiling above 170°. Mansfield (ii. 207) obtained it from the portion boiling between 170° and 180°. Berthelot (*Bull. Soc. Chim.* [2] viii. 226) separated by fractional distillation the portion of heavy coal-tar oil boiling between 175° and 190°; then (after mixing the distillate with the liquid remaining in the retort and the portion saturated with naphthalene) collected by a second fractionation the portion distilling between 178° and 180°, and separated the naphthalene therefrom by means of an alcoholic solution of picric acid. The oil separated from the alcoholic mother-liquid by ammoniacal water yielded, after repeated rectification, a hydrocarbon $C^{10}H^{14}$, boiling between 179° and 180°, and yielding with nitric and sulphuric acids the usual reactions of the aromatic hydrocarbons. Heated with 80 times its weight of saturated aqueous hydriodic acid, it yielded decane or decyl-hydride, $C^{10}H^{22}$, together with a small quantity of a very volatile hydride, [C^8H^{14}?]. Rommier (*Compt. rend.* lxviii. 1482), by treating the portion of coal-tar oil distilling between 200° and 220° with fuming nitric acid, obtained a small quantity of hard colourless crystals having approximately the composition of *dinitrocymene*, $C^{10}H^{12}(NO^2)^2$.

β cymene differs from α cymene in its boiling point. Its products of oxidation do not appear to have been examined; but as products of destructive distillation have hitherto been found to yield only methyl-derivatives of benzene, it most probably consists of tetramethylbenzene.

AZOCYMENE, $C^{20}H^{26}N^2$, is formed by the action of sodium-amalgam on nitrocymene (from the cymene of Roman cumin-oil), and crystallises in cherry-coloured plates melting at 86° (Werigo, *Zeitschr. Ch. Pharm.* 1864, p. 721).

Hydrocarbons $C^{11}H^{16}$.

Of the seven metameric forms of this hydrocarbon, viz. $C^6H^5.C^5H^{11}$; $C^6H^4.C^3H^7.C^2H^5$; $C^6H^4.C^4H^9.CH^3$; $C^6H^3.C^3H^7.(CH^3)^2$; $C^6H^3.(C^2H^5)^2.CH^3$; $C^6H^2.(C^2H^5)(CH^3)^3$; and $C^6H.(CH^3)^5$, the three following are known:

1. **Amyl-benzene.** $C^6H^5.C^5H^{11}$.—Obtained by the action of sodium on a mixture of bromobenzene and amyl bromide diluted with an equal volume of ether (Tollens a. Fittig, *Ann. Ch. Pharm.* cxxxi. 303). It has a peculiar odour, not like that of benzene, a sp. gr. of 0·859 at 12°, and boils at 193° (Bigot a. Fittig, *ibid.* cxli. 160). By oxidation with chromic acid, it yields benzoic acid, together with other acids not yet investigated (Tollens a. Fittig). With 2 at. bromine it forms a liquid compound in which a few crystals gradually appear; on mixing the well-cooled hydrocarbon with 4 at. bromine, and heating the mixture to 100° till it is decolorised, the contents of the tube solidify to a crystalline pulp of *tribromamylbenzene*, $C^{11}H^{13}Br^3$. This compound crystallises from hot alcohol in silky needles, slightly soluble in cold, easily in hot alcohol, melting at 140° and decomposing at a slightly higher temperature. With *chlorine* and with fuming *nitric acid*, amylbenzene forms only liquid compounds. Concentrated *sulphuric acid* converts it into a very stable, crystallisable, deliquescent sulpho-acid, whose barium salt, $(C^{11}H^{15}SO^3)^2Ba$, crystallises readily in long needles very slightly soluble in cold water. The *potassium salt* $C^{11}H^{15}SO^3K$ is a radio-crystalline mass very soluble in water and in alcohol (Tollens a. Fittig).

2. **Diethyl-methyl-benzene** or **Diethyl-toluene.** $C^6H^3\left\{\begin{matrix}(CH^3)\\(C^2H^5)^2\end{matrix}\right.$ (Lippmann a. Louguinine, *Bull. Soc. Chim.* [2] viii. 426).—Produced by the action of zinc-ethyl on benzylene chloride:

$$C^6H^5.CHCl^2 + Zn(C^2H^5)^2 = ZnCl^2 + C^6H^3.CH^3(C^2H^5)^2.$$

To moderate the violence of the reaction, it is best to dilute the mixture with five times its weight of benzol, and gradually add the well-cooled solution of the benzylene chloride to the solution of the zinc-ethyl in excess. At the end of the reaction, the white solid product saturated with benzol is treated with hydrochloric acid, and the separated oily layer, after drying with calcium chloride, is freed from benzol by distillation. The remaining hydrocarbon, after repeated heating with sodium to 200° for several days, and final rectification, yields, in the portion boiling between 175° and 180°, pure diethyl-toluene as a colourless aromatic liquid, of sp. gr. 0·8751 at 0°, boiling at 178° (i.e. 15° lower than amyl-benzene), and having a vapour-density of 5·1245, or by calculation 5·1107.

3. **Propyl-dimethyl-benzene, Propyl-xylene,** or **Laurene.** $C^6H^3\left\{\begin{matrix}(CH^3)^2\\ C^3H^7\end{matrix}\right.$ (Fittig, Kõbrich a. Jilke, *Ann. Ch. Pharm.* cxlv. 129; *Jahresb.* 1867, p. 701).—Produced, together with several of its lower homologues, by distilling camphor with fused zinc chloride, passing over between 185° and 188°. It has a sp. gr. of 0·887 at 10°, and boils when pure at 188°. In contact with 6 at. bromine, it is gradually converted into *tribromolaurene*, $C^{11}H^{13}Br^3$, which crystallises from hot alcohol in long needles melting at 125°; not decomposed by alcoholic potash at the boiling heat. With a mixture of nitric and sulphuric acids laurene forms a nitro-compound melting at 84°. Dilute nitric acid oxidises it to *lauroxylic acid*, $C^9H^{10}O^2$, an acid isomeric with xylic acid:

$$\underset{\text{Laurene.}}{C^6H^3\left\{\begin{matrix}(CH^3)^2\\ C^3H^7\end{matrix}\right.} + O^6 = \underset{\text{Lauroxylic acid.}}{C^6H^3\left\{\begin{matrix}(CH^3)^2\\ CO^2H\end{matrix}\right.} + 2CO^2 + 3H^2O.$$

By chromic acid it is further oxidised, acetic acid being produced, apparently as the ultimate product of its oxidation.

The hydrocarbon $C^{12}H^{18}$, of which ten modifications are possible, is known in only one, viz.,

Amyl-methyl-benzene or **Amyl-toluene.** $C^6H^4\left\{\begin{matrix}CH^3\\ C^5H^{11}\end{matrix}\right.$ (Bigot a. Fittig, *Ann. Ch. Pharm.* cxli. 160).—Prepared similarly to amyl-benzene (p. 303), excepting that the weighed quantity of sodium is added in the first place to the ether which serves as a diluent, and then, when all evolution of hydrogen has ceased, the thoroughly dried mixture of bromotoluene and amyl bromide is added. It is a colourless liquid, having an agreeable odour like that of ethyl-benzene, of sp. gr. 0·8643 at 9°, boiling at 213°, and not solidifying at −20°. By oxidation with chromic acid it yields acetic and terephthalic acids:

$$C^6H^4\left\{\begin{matrix}CH^3\\ C^5H^{11}\end{matrix}\right. + O^{10} = C^6H^4\left\{\begin{matrix}CO^2H\\ CO^2H\end{matrix}\right. + 2C^2H^4O^2 + 2H^2O.$$

Heated with 8 at. bromine to 100°, it forms *tribromamyl-toluene*, $C^{12}H^{15}Br^3$, as a viscid ropy mass, which becomes mobile at 100°, and decomposes at a higher temperature. Fuming nitric acid converts it in the cold into dinitro-amyltoluene, $C^{12}H^{16}(NO^2)^2$, a viscid yellow transparent liquid, insoluble in water, easily soluble in alcohol, and not capable of distilling without decomposition. It does not appear to yield a solid trinitro-compound. It dissolves in fuming sulphuric acid, forming *amyltoluene-sulphuric acid*, $C^{12}H^{17}SO^3H$, the barium salt of which is very soluble in water and alcohol, and uncrystallisable; the potassium salt, $C^{12}H^{17}SO^3K$, likewise easily soluble and not obtainable in distinct crystals.

The hydrocarbon $C^{13}H^{20}$ is likewise known in only one modification, viz.,

Amyl-dimethyl-benzene or **Amyl-xylene,** $C^6H^3\left\{\begin{matrix}(CH^3)^2\\ C^5H^{11}\end{matrix}\right.$, which is prepared similarly to amyl-toluene. It is a liquid smelling very much like amyl-benzene and amyl-toluene, boiling at 232°–233°, and having a sp. gr. of 0·8951 at 9°. It does not yield any well-characterised bromo- or nitro- derivatives. Fuming sulphuric acid dissolves it readily, forming *amylxylene-sulphuric acid*, $C^{13}H^{19}SO^3H$, the barium and potassium salts of which are very soluble and not crystallisable (Bigot a. Fittig, *loc. cit.*).

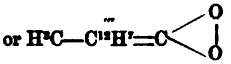
BENZERYTHRENE. A solid hydrocarbon of unknown composition, formed, together with chrysene and other hydrocarbons, solid, liquid, and gaseous, when benzene vapour is passed through a porcelain tube heated to bright redness; occurring also amongst the solid hydrocarbons which pass over after the naphthalene in the distillation of coal-tar, the last portions of this distillate consisting of chrysene and benzerythene. Still more abundantly do these two hydrocarbons occur in the reddish-yellow product obtained by the destructive distillation of the dry pitch of fir-wood.

Benzerythrene is at ordinary temperatures an orange-yellow resinous body of the consistence of colophony, and distilling at a red heat in yellow vapours. It dissolves but sparingly in alcohol, even at the boiling heat, forming a solution which gives no precipitate with picric acid, but when heated with this acid to the boiling point deposits on cooling brownish-yellow flocks, consisting of benzerythrene picrate (Berthelot, *Jahresb.* 1866, p. 541; 1867, pp. 599, 605).

BENZEUGENYL. Syn. with EUGENO-BENZOIC ANHYDRIDE (ii. 605).

BENHYDROL. $C^{13}H^{12}O$.—A monatomic alcohol produced by the action of nascent hydrogen on benzophenone or phenylbenzoyl, $C^6H^5.C^7H^5O$, under which it is described (iv. 478).

BENZIDINE or **DIAMIDO-DIPHENYL.** $C^{12}H^8(NH^2)^2$.—See i. 514; iv. 411. A base, $C^{14}H^{16}N^2$, homologous with benzidine, is produced by the action of hydrochloric acid on an alcoholic solution of hydrazotoluide. It crystallises in silvery laminæ easily soluble in boiling water, soluble in alcohol and ether, melting at 128°–129°, and decomposing at a higher temperature. It is a bi-acid base, forming a neutral and an acid sulphate; the latter, $C^{14}H^{16}N^2.2H^2SO^4$, is a pulverulent salt partially decomposed by water. The *dihydrochloride*, $C^{14}H^{16}N^2.2HCl$, crystallises in colourless laminæ easily soluble in water, and forms a yellow crystalline precipitate with platinic chloride (Petrieff, *Zeitschr. f. Chem.* [2] vi. 265).

BENZILE or **BENZILIC ANHYDRIDE.** $C^{14}H^{10}O^2$ or 
$H^3C—\overset{'''}{C^{12}H^7}=C<\begin{matrix}O\\|\\O\end{matrix}$

(see AROMATIC SERIES, p. 211).—This body, originally obtained by oxidation of benzoïn, $C^{14}H^{12}O^2$, appears also to be produced by heating bromotoluylene with water to 150° (Limpricht a. Schwarert, *Jahresb.* 1867, p. 674):

$$\underset{\text{Bromotoluylene.}}{3C^{14}H^{11}Br} + 2H^2O = \underset{\text{Benzile.}}{C^{14}H^{10}O^2} + \underset{\text{Toluylene.}}{2C^{14}H^{12}} + 3HBr.$$

The benzile thus obtained crystallised in four-sided needles melting at 95° (Zinin's benzile, i. 515, melts at 90°–92°, and crystallises in six-sided prisms). The hexagonal crystals possess an optical rotatory power rather greater than that of quartz. All the crystals examined were dextrogyrate. Their double refraction is positive and very strong. For the line D, at 14°, $\omega = 1{\cdot}6588$ and $\epsilon = 1{\cdot}6784$. They expand by heat nine times as much as platinum in the direction of the axis, and five times as much in the direction perpendicular to the axis. Hence, contrary to what takes place in quartz, the original rhombohedron of 80° 14′ is rendered more acute by rise of temperature (Descloizeaux, *Compt. rend.* lxviii. 308).

Chlorobenzile. $C^{14}H^{10}OCl^2$ (Zinin, *Ann. Ch. Pharm.* cxix. 177; *Zeitschr. f. Chem.* [2] iv. 718).—When benzile is heated to fusion with phosphorus pentachloride, 2 at. chlorine take the place, not of hydrogen, but of 1 at. oxygen, forming chlorobenzile:

$$C^{14}H^{10}O^2 + PCl^5 = POCl^3 + C^{14}H^{10}OCl^2.$$

On expelling the phosphorus oxychloride by heat, and washing the residue first with hot and then with cold water, it solidifies to a white crystalline mass of chlorobenzile. This substance dissolves easily in ether, and crystallises therefrom in short rhombic prisms or thin rhombic tables; it is less soluble in alcohol, insoluble in water; melts at 71°, and solidifies in the crystalline form (unless it has been too strongly heated or fused under water or alcohol, in which case it remains liquid at a lower temperature); it is decomposed by distillation, yielding a liquid containing benzoyl chloride. It dissolves with rise of temperature in strong *nitric acid*; and by boiling with this acid, or with an alcoholic solution of silver nitrate, it is converted, with evolution of red vapours, into benzile, which separates on addition of water. Heated with *water* in sealed tubes to 180°, it is completely resolved into benzile and hydrochloric acid:

$$C^{14}H^{10}OCl^2 + H^2O = C^{14}H^{10}O^2 + 2HCl.$$

Alcohol decomposes it at a lower temperature, yielding benzile, ethyl chloride, and hydrochloric acid:

$$C^{14}H^{10}OCl^2 + C^2H^6O = C^{14}H^{10}O^2 + C^2H^5Cl + HCl.$$

Alcoholic potash acts on chlorobenzile in alcoholic solution, slowly in the cold, more quickly and completely when heated, forming potassium benzoate and benzoic aldehyde:

$$C^{14}H^{10}OCl^2 + 3KOH = C^7H^5KO^2 + C^7H^6O + 2KCl + H^2O.$$

Aqueous *ammonia* does not act on chlorobenzile; alcoholic ammonia decomposes it in a more complex manner. Chlorobenzile heated to 200° with an equivalent quantity of *phosphorus pentachloride* is converted into a body $C^{14}H^{10}Cl^4$, which is insoluble in water, slightly soluble in alcohol and ether, and is slowly converted by nitric acid into a nitro-compound. In boiling alcoholic solution, it is easily coverted by sodium-amalgam into a hydrocarbon $C^{14}H^{10}$, identical with tolane. Chlorobenzile treated in alcoholic solution with zinc and hydrochloric acid is quickly converted into deoxybenzoïn:

$$C^{14}H^{10}OCl^2 + 2HCl + Zn^2 = 2ZnCl^2 + C^{14}H^{12}O.$$

Nitrobenzile. $C^{14}H^9(NO^2)O^2$ (Zinin, *Ann. Ch. Pharm. Suppl.* iii. 153).—Produced, together with nitrobenzoic acid and a small quantity of benzile, by prolonged boiling of deoxybenzoïn with nitric acid of sp. gr. 1·2; more advantageously prepared by adding benzoïn (not more than 10 grms.) to nitric acid of sp. gr. 1·5 cooled to 0°, and immediately pouring the resulting solution into cold water. The colourless body thereby separated dissolves in an equal weight of ether, and separates therefrom in sulphur-yellow granules, composed of laminæ and needles, which are now much less soluble in ether, still less in alcohol, and quite insoluble in water. The nitrobenzile, purified by recrystallisation, first from ether and alcohol, then from strong nitric acid, and lastly from pure alcohol, melts at 110°, distils with partial decomposition, dissolves in 30 pts. of boiling alcohol of 85 p. c., and in 27 pts. of 92 p. c. alcohol. When its hot saturated alcoholic solution is mixed with sufficient *alcoholic potash* to produce a faint alkaline reaction, potassium azobenzoate separates on cooling, and oxybenzoate remains in solution:

$$\underset{\text{Nitrobenzile.}}{C^{14}H^9NO^4} + 2KHO = \underset{\text{Azobenzoate.}}{C^7H^4KNO^2} + \underset{\text{Oxybenzoate.}}{C^7H^5KO^3} + H^2O.$$

Hydrobenzile, $C^{14}H^{12}O$, produced by the action of ammonium sulphide on benzile, is described in vol. iii. p. 185.

BENZILIC ACID. $C^{14}H^{12}O^3 = \overset{'''}{C^{12}H^7}\left\{\begin{array}{l}OH\\ CO^2H.\\ CH^3\end{array}\right.$ (See AROMATIC SERIES, p. 211.)—This acid, originally obtained by oxidation of benzoïn (i. 515), is also produced by boiling that substance with alcoholic potash:

$$C^{14}H^{12}O^2 + KHO = C^{14}H^{11}KO^3 + H^2,$$

the hydrogen being oxidised in contact with the air. If, however, the benzoïn be heated with alcoholic potash to 120°–160° in a sealed tube exhausted of air, it is converted into benzilic acid, hydrobenzoïn, $C^{14}H^{14}O^2$, and a body crystallising in needles, which Claus obtained by the action of sodium-amalgam on an ethereal solution of bitter almond oil (Zinin, *Bull. Soc. Chim.* [2] vii. 260). According to Borodine (*Rép. Chim. pure*, iv. 433), benzilic acid is produced by the action of sodium amylate on benzile.

Pure benzilic acid melts at 150°. When heated for some time to 180° it yields, together with a red resin, a substance having the composition $C^{28}H^{22}O^5$, according to the equation $2C^{14}H^{12}O^3 - H^2O = C^{28}H^{22}O^5$. This substance crystallises in small needles melting at 196°, and is reconverted into benzilic acid by heating with water to 180°. Benzilic acid heated with *potassium chromate and dilute sulphuric acid* is resolved into water, carbon dioxide, and benzophenone:

$$C^{14}H^{12}O^3 + O = H^2O + CO^2 + C^{13}H^{10}O.$$

Heated with *hydriodic acid* to 180°, it forms an acid which crystallises in beautiful needles, melts at 146°, and has the composition $C^{14}H^{12}O^2$ (A. Jena, *Berlin. Chem. Gesellsch.* 1869, p. 384).

BENZOIC ACID. $C^7H^6O^2 = C^6H^5.CO^2H$.—This acid has been produced synthetically by four different processes: 1. By passing benzene vapour mixed with carbonyl chloride (phosgene) through a heated retort exposed to the sun's rays, whereby benzoyl chloride, $C^6H^5.COCl$, is produced:

$$C^6H^6 + COCl^2 = HCl + C^6H^5.COCl,$$

and decomposing the latter with water (Harnitz-Harnitzky, *Bull. Soc. Chim.* [2] i. 322). According to Berthelot, this reaction does not take place (p. 262). On the other hand, Schützenberger has obtained benzoic acid by treating benzene with a mixture of sulphuric anhydride and carbon tetrachloride (which produces carbonyl chloride); and Wurtz has formed it by the action of ethyl chlorocarbonate and sodium-amalgam on chlorobenzene (p. 206).

2. By adding sodium in small pieces to monobromobenzene diluted with benzene in a long-necked retort provided with an ascending condensing tube, heating the retort in the water-bath, and passing a current of dry carbonic acid gas into the mixture:

$$\underset{\text{Bromobenzene.}}{C^6H^5Br} + Na^2 + CO^2 = NaBr + \underset{\text{Sodium benzoate.}}{C^6H^5.CO^2Na}$$

The product is treated with water which dissolves the sodium benzoate (Kekulé, *Ann.*

Ch. Pharm. cxxxvii. 129). This process is applicable also to the preparation of the homologues of benzoic acid (p. 205).

3. By distilling aniline with oxalic acid, whereby, amongst other products, benzonitrile, $C^6H^5.CN$, is obtained, and decomposing this compound with potash (Hofmann, *Proc. Roy. Soc.* xvi. 484). See Aromatic Series (p. 206). V. Merz (*Zeitschr. f. Chem.* [2] iv. 33) obtains benzonitrile by heating potassium benzene-sulphate with potassium cyanide:

$$C^6H^5.SO^3K + CNK = SO^3K^2 + C^6H^5.CN,$$

and converts the nitrile into benzoic acid by distillation with alcoholic potash.

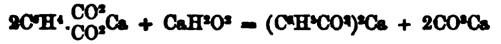
4. By the action of a mixture of manganese dioxide and dilute sulphuric acid on benzene, the reaction consisting, first in the production of formic acid by oxidation of a portion of the benzene; secondly in the abstraction of an atom of hydrogen from the former and from the benzene residue by oxidation, and in the union of the residues CO^2H and C^6H^5 to form benzoic acid:

$$C^6H^6 + H.CO^2H + O = H^2O + C^6H^5.CO^2H.$$

Part of the benzoic acid is, however, converted by a repetition of the same reaction into phthalic acid, $C^6H^4.(CO^2H)^2$ (Carius, *Ann. Ch. Pharm.* cxlviii. 50, 99).

The following modes of formation have also been observed; the fifth and sixth are applied to the industrial preparation of benzoic acid:

5. By heating phthalic acid with an equivalent quantity of calcium hydrate (slaked lime) to 330°–350° for several hours, excluding the air as much as possible:



$$2C^6H^4.\genfrac{}{}{0pt}{}{CO^2}{CO^2}Ca + CaH^2O^2 = (C^6H^5CO^2)^2Ca + 2CO^3Ca$$

Phthalate. Hydrate. Benzoate. Carbonate.

The phthalic acid required for this process is prepared from naphthalene (P. a. E. Depouilly, *Bull. Soc. Chim.* [2] iii. 163, 469).

6. By boiling benzoyl chloride, $C^6H^5.CO^2Cl$, with nitric acid for several hours in a flask connected with an inverted Liebig's condenser, whereby it is oxidised to benzoic acid and benzoic aldehyde, which may be separated by water. The benzoic acid thus obtained has a strong odour of bitter almond oil, which it partly loses on exposure to the air (Lauth a. Grimaux, *ibid.* vii. 105).

7. By exposing benzylene chloride, $C^7H^6Cl^2$, to the joint action of air and water (Carius, *Compt. rend.* lvi. 222).

8. By heating benzyl disulphide to 130° with bromine and water (Märcker, *Ann. Ch. Pharm.* cxl. 86):

$$C^{14}H^{14}S^2 + 4H^2O + 5Br^2 = 2C^7H^6O^2 + 10HBr + S^2.$$

9. By the oxidation of certain aromatic hydrocarbons, viz. those which contain a single lateral chain, e.g. methyl-benzene, ethyl-benzene, &c. See Aromatic Series, p. 200.

10. By the action of sodium-amalgam and water on amidobenzoic acid (Hübner a. Petermann, *Zeitschr. f. Chem.* [2] iv. 548).

$$C^6H^4NH^2.CO^2H + H^2 = NH^3 + C^6H^5.CO^2H.$$

11. By boiling diazosalyl-nitric acid (prepared from anthranilic acid by the action of nitrous acid) in alcoholic solution (Griess, *ibid.* ii. 157):

$$(C^7H^4N^2O^2)^2.NHO^3 + 2C^2H^6O = 2C^7H^6O^2 + 2C^2H^4O + NHO^3 + N^4.$$

Diazosalyl-nitric acid. Alcohol. Benzoic acid. Aldehyde.

12. By heating quinic acid with saturated hydriodic acid to 115°–120°, or by distilling its syrupy solution with 4 mol. phosphorus diniodide. If the quinic acid be heated to 140° with hydriodic acid and phosphorus (the presence of which prevents the separation of iodine), an acid is formed containing more hydrogen than benzoic acid: hence the reduction appears to take place as follows:

$$C^7H^{12}O^6 + 8HI = C^7H^{12}O^2 + 4H^2O + 4I^2$$

and

$$C^7H^{12}O^2 + 3I^2 = C^7H^6O^2 + 6HI$$

(Lautemann, *Ann. Ch. Pharm.* cxx. 9).

13. By heating the aurochloride of cocaine or of atropine (Niemann, *Jahresb.* 1860, p. 367).

Decompositions.—1. A hot solution of benzoic acid acidulated with hydrochloric acid is decomposed by *sodium-amalgam* into benzyl alcohol, C^7H^8O, a neutral crystallising oil, $C^{14}H^{16}O^2$, and benzoleic acid, $C^7H^{10}O^2$, a volatile acid heavier than water and smelling like valerianic acid (Kolbe, *Ann. Ch. Pharm.* cxviii. 122; M. Hermann, *ibid.* cxxxii. 75).

2. Benzoic acid heated with 80 pts. of saturated *hydriodic acid* yields septane or heptyl hydride, C^7H^{16}, as normal product, and sextane, C^6H^{14}, resulting from the splitting up of the benzoic acid into benzene and carbon dioxide (Berthelot, *Jahresb.* 1867, p. 346).

3. Passed in vapour over heated zinc-dust, it is reduced to benzoic aldehyde (Baeyer, *Ann. Ch. Pharm.* cxl. 295).

4. When a solution of benzoic acid is boiled with *lead dioxide*, and *dilute sulphuric acid* is gradually added, the benzoic acid is oxidised to succinic acid. The same transformation takes place in the animal organism (Meissner a. Shepard, *Jahresb.* 1866, p. 397).

5. Iodine monochloride decomposes aqueous benzoic acid, with separation of iodine and formation of chlorinated benzoic acid (Stenhouse, *Chem. Soc. J.* [2] i. 327, 366).

6. Brown *chloride of sulphur*, (SCl^2), acts violently on dry benzoic acid, forming benzoyl chloride, together with sulphurous oxide and hydrochloric acid. (See SULPHUR, CHLORIDES OF, v. 535).

Metallic Benzoates. The *ammonium salt* $C^7H^5O^2(NH^4)$ crystallises in tabular rhombic combinations, $oP . P . \infty\breve{P} . \bar{P}\infty$; angle P : P (macr.) = 24° 28′; P : P (brach.) = 96° 12′; P : P (basal.) = 143° 56′; $\bar{P}\infty : \bar{P}\infty$ (basal.) = 130° 51′ (Marignac, *Compt. rend.* xlv. 650). The *potassium salt* $C^7H^5O^2K$ is probably isomorphous with the ammonium salt, but it crystallises in laminæ the form of which cannot be exactly defined (Marignac). Treated with cyanogen bromide, it yields large quantities of carbon dioxide and benzonitrile (together with a neutral solid azotised body):

$$C^7H^5O^2K + CNBr = CO^2 + KBr + C^7H^5N$$

(Cahours, *Ann. Ch. Phys.* [3] lii. 201). Subjected to electrolysis in neutral solution, it yields potash at the negative, benzoic anhydride and oxygen at the positive pole:

$$2C^7H^5O^2K = \underbrace{(C^7H^5O)^2O + O}_{+} \ldots + \underset{-}{\underline{K^2}}.$$

In a solution containing a slight excess of potash, $4C^7H^5O^2K + KHO$, the same decomposition takes place, but acetylene is also given off, part of the benzoic acid being decomposed as shown by the equation:

$$C^7H^6O^2 + O^7 = C^2H^2 + 3CO + 2CO^2 + 2H^2O.$$

In a very alkaline solution, nothing is evolved at the positive pole but oxygen, with small quantities of carbon monoxide and dioxide (E. Bourgoin, *Zeitschr. f. Chem.* [2] iv. 566).

Sodium Benzoate, $C^7H^5O^2Na$, is decomposed by iodine monochloride at ordinary temperatures, forming iodine benzoate or benzo-iodic acid: $C^7H^5O^2Na + ICl = NaCl + C^7H^5IO^2$. On heating the product, carbon dioxide and iodine are evolved, together with an oily liquid which is resolved by fractional distillation into monoiodobenzene, C^6H^5I, boiling at 185°, and di-iodobenzene, $C^6H^4I^2$, solidifying at ordinary temperatures, and boiling at 250° (Schützenberger, *Rép. Chim. pure*, iii. 145; iv. 268).

Cerous Benzoate, $(C^7H^5O^2)^2Ce . 2H^2O$, obtained by precipitating cerous sulphate with ammonium benzoate, is a granular crystalline powder soluble in acids and in cerous sulphate, sparingly soluble in water (Czudnowicz, *Jahresb.* 1861, p. 190). The *lanthanum salt* $(C^7H^5O^2)^2La . 2H^2O$ is a crystallo-granular precipitate, slightly soluble in water, becoming anhydrous at 100° (Czudnowicz, *ibid.* 1860, p. 129).

Chromic Benzoates.—Chromic salts mixed with potassium benzoate yield gradually at ordinary temperatures, immediately at 40°–50°, a precipitate probably consisting of the normal salt $(Cr^2)^{vi}(C^7H^5O^2)^6 . \frac{1}{2}H^2O$. Boiled with water or alcohol, it gives up benzoic acid and yields the basic salt $\left.\begin{array}{r}(C^7H^5O^2)^4\\(HO)^2\\(Cr^2)^{vi}\end{array}\right\}O^6 . H^2O$ (Schiff, *Ann. Ch. Pharm.* cxxiv. 157).

Alcoholic Benzoates. Benzoic Ethers. *Methyl Benzoate*, $C^7H^5O^2 . CH^3$, has, according to Mendelejef (*Jahresb.* 1860, p. 7), a sp. gr. of 1·0921 at 12·3°. By prolonged digestion at 100° with potassium dichromate and dilute sulphuric acid, it is oxidised to benzoic acid, formic acid, and carbon dioxide (R. H. Smith, *Chem. Soc. J.* [2] v. 131).

Ethyl Benzoate. $C^7H^5O^2 . C^2H^5$.—Sp. gr. 1·0517 at 14·1° (Mendelejef). By oxidation with chromic acid mixture it yields benzoic and acetic acids (Smith). Heated with bromine, ultimately to 270°, it yields benzoic acid and ethylene bromide (A. Naumann, *Ann. Ch. Pharm.* cxxxiii. 199):

$$C^7H^5O^2.C^2H^5 + Br^2 = C^7H^6O^2 + C^2H^4Br^2.$$

According to Geuther (*Zeitschr. f. Chem.* [2] iv. 658), ethyl benzoate is not attacked by sodium ethylate at 120°; but at 160° sodium benzoate and ethyl oxide are formed, together with a colourless liquid, $C^7H^{16}O$, and a solid yellow mass, $C^7H^{16}O$.

Amyl Benzoate, $C^7H^5O^2.C^5H^{11}$, is formed by heating ethyl benzoate with amyl alcohol to 217°–240° for sixty hours, the ethyl and amyl changing places. A mixture of 1 mol. ethyl benzoate and 1 mol. amyl acetate heated for several hours to 300° yielded only small quantities of ethyl acetate and amyl benzoate (Friedel a. Crafts, *Bull. Soc. Chim.* [2] ii. 100).

Cetyl Benzoate, $C^7H^5O^2.C^{16}H^{33}$ (i. 840).

Cholesteryl Benzoate, $C^7H^5O^2.C^{26}H^{43}$ (i. 926).

Sycoceryl Benzoate, $C^7H^5O^2.C^{18}H^{29}$ (v. 646).

Propylene or *Tritylene Benzoate*, $(C^7H^5O^2)^2.C^3H^6$, prepared by heating silver benzoate with propylene bromide, and treating the product with sodium carbonate and ether, forms large colourless crystals isomorphous with those of ethylene benzoate; insoluble in water and alkaline carbonates, soluble in ether and in alcohol, melting at 72°, and volatilising without decomposition at a temperature above 300°. *Amylene benzoate*, $(C^7H^5O^2)^2.C^5H^{10}$, prepared in like manner crystallises in long shining laminæ melting at 123° (A. Mayer, *Bull. Soc. Chim.* [2] ii. 451).

Benzylene Benzoate, $(C^7H^5O)^2.C^7H^6$ (i. 578).

Cumylene Benzoate, $(C^7H^5O^2)^2.C^{10}H^{12}$ (ii. 184).

The chlorinated, brominated derivatives, &c., of benzoic acid exhibit isomeric modifications according to the relative positions occupied by the chlorine, bromine, &c., and the radicle CO^2H of the benzoic acid.

Bromobenzoic Acids.

Monobromobenzoic acid, $C^6H^4Br.CO^2H$, is produced by heating benzoic acid with bromine and water to 100° for several days. The acid thus obtained is slightly soluble in boiling water, dissolves easily in dilute alcohol, and crystallises in flat needles, melting at 152°–153°. Its *calcium salt*, $(C^7H^4BrO^2)^2Ca.3H^2O$, crystallises from water or alcohol in nodular groups of ill-defined needles. The *barium salt* $(C^7H^4BrO^2)^2Ba.4H^2O$ forms sparingly soluble flat needles. The acid is converted by *nitric acid* into two isomeric nitrobromobenzoic acids; by further treatment with *bromine*, into tribromobenzoic acid; by *potassium chlorate* and *hydrochloric acid*, into chlorobenzoic acid. Its silver salt exposed to the action of bromine-vapour yields a gas, probably O or Br^2O, together with bromobenzoic anhydride, which is converted by water into bromobenzoic acid:

$$2C^7H^4BrAgO^2 + 2Br^2 = (C^7H^4BrO)^2O + 2AgBr + Br^2O$$

(Reinecke, *Zeitschr. f. Chem.* [2] v. 109).

Bromobenzoic acid is also formed, together with hydrobromide of amidobenzoic acid, by the action of hydrobromic acid on diazobenzo-amidobenzoic acid (Griess, iv. 292):

$$C^7H^4N^2O^2.C^7H^7NO^2 + 2HBr = C^7H^5BrO^2 + C^7H^7NO^2.HBr + N^2.$$

The bromobenzoic acid thus produced appears to be identical with that obtained directly from benzoic acid. Diazobenzo-amidobenzoic acid treated with bromine and water yields a monobromobenzoic acid, which crystallises in laminæ, and appears to be different from the preceding (Griess). Bromobenzoic acid identical with the first is also produced by oxidising orthobromotoluene with chromic acid mixture (Wroblewsky, *Zeitschr. f. Chem.* [2] v. 332): hence this modification consists of orthobromobenzoic acid. The same acid is obtained by decomposing with boiling alcohol the perbromide of diazobenzoic acid obtained by mixing nitrate of diazobenzoic acid with a solution of bromine in hydrobromic acid (Griess, *Jahresb.* 1865, p. 337):

$$C^7H^4N^2O^2.HBr.Br^2 = C^7H^5BrO^2 + N^2 + Br^2;$$

and by the action of bromine-vapour on silver-benzoate (i. 314). Benzamide boiled with bromine and water is resolved, according to the equation,

$$C^7H^7NO + H^2O + Br^2 = C^7H^5BrO^2 + NH^4Br,$$

into ammonium bromide and bromobenzoic acid, which, however, appears to be a mixture of two isomeric acids, inasmuch as its melting point rises by recrystallisation from 149° to nearly 200° (Reinecke, *Zeitschr. f. Chem.* [2] ii. 367).

Bromobenzoic acid distilled with lime yields pure benzene; when distilled with pumice it passes over undecomposed (Riche, *Compt. rend.* liii. 586). The ammoniacal solution of the acid (prepared by Peligot's process, i. 554) is converted by heat into amidobenzoic acid: $C^7H^5BrO^2 + NH^3 = HBr + C^7H^4(NH^2)O^2$ (Alexeyeff, *Bull. Soc. Chim.* 1861, p. 71). Sodium bromobenzoate distilled with an equivalent quantity of iodine monochloride gives off carbon dioxide, iodine, bromobenzoic acid, and an oil containing iodobenzene and apparently phenyl bromobenzoate, $C^7H^4BrO^2.C^6H^5$ (Schützenberger a. Segenwald, *Jahresb.* 1862, p. 250).

Metabromobenzoic or *Bromosalylic acid*, $C^6H^3BrH.CO^2H$, is said by v. Richter (*Zeitschr. f. Chem.* [2] v. 457) to be produced, together with the ortho-acid, by heating benzoic acid with water and bromine. It is said to be less soluble than the ortho-acid, and to separate out nearly pure, when the hot aqueous solution of the two is left to cool, in white flocks melting at 90°, and subliming at 89° in needles. These results, however, do not appear to be very well established (comp. Hübner, *ibid.* 514). Hübner a. Petermann (*Ann. Ch. Pharm.* cxlix. 131) find that only one monobromobenzoic acid is formed by the action of bromine on benzoic acid.

Parabromobenzoic or *Bromodracylic Acid*, $C^6H^2BrH^2.CO^2H$, obtained by oxidising bromotoluene with chromic acid, crystallises from ether in small volatile needles, melting at 251°, slightly soluble in cold, more soluble in boiling water, easily in alcohol and ether. Its easily soluble *barium salt*, $(C^7H^4BrO^2)^2Ba$, crystallises in nacreous laminæ; the *silver salt* $C^7H^4BrO^2Ag$ in white slightly soluble needles. The ethylic ether is a fragrant liquid (Hübner a. Ohly, *Jahresb.* 1866, p. 347).

Dibromobenzoic acid, $C^7H^4Br^2O^2 = C^6H^3Br^2.CO^2H$, is formed, together with other bromobenzoic acids, when benzoic acid is strongly heated with excess of bromine (Reinecke, *Jahresb.* 1865, p. 322; Hübner, *loc. cit.*). It crystallises in short needles melting at 223°-227°, sparingly soluble in cold water, easily in alcohol and ether, not volatilising with aqueous vapour. The *barium salt* $(C^7H^3Br^2O^2)^2Ba.2H^2O$ forms short, transparent needles; the *calcium salt*, shining laminæ; the *sodium salt* is difficult to crystallise (Hübner).

Dibromodracylic acid, which sublimes in needles, is produced by the action of nitrous acid on a hot alcoholic solution of dibromamidodracylic acid (Geitner a. Beilstein, *Jahresb.* 1865, p. 335).

Tribromobenzoic acid, $C^7H^3Br^3O^2 = C^6H^2Br^3.CO^2H$, is formed from the monobrominated acid when the mixture of benzoic acid with bromine and water is heated to 140°-160°, part of it being, however, converted into pentabromobenzoic acid. The tribrominated acid may be partly separated by dissolving the mixture of acids which crystallises out, in a boiling solution of sodium acetate, the liquid on cooling yielding crystals of the tribrominated acid (Reinecke). It is also formed, together with monobromobenzoic acid, by the action of bromine and water on diazobenzo-amidobenzoic acid (Griess). It crystallises in tufts of slender needles having a strong silky lustre, and melting at 234°-235°; the admixture of another bromobenzoic acid, however, lowers the melting point to below 100°. The crystals are nearly insoluble in boiling water, more easily in dilute alcohol or boiling benzene. The metallic *tribromobenzoates* are sparingly soluble, and crystallise in needles. The calcium salt $(C^7H^2Br^3O^2)Ca.5H^2O$ easily gives off its water when heated.

Tribromobenzoic acid is the most stable of all the bromobenzoic acids, not being altered by boiling with nitric acid or by fusion with caustic potash. By prolonged heating in a sealed tube with potassium chlorate and hydrochloric acid it is completely converted into trichlorobenzoic acid. The silver salt $C^7H^2Br^3O^2Ag$, exposed to the action of bromine vapour [? moist], is ultimately reconverted into tribromobenzoic acid (Reinecke, *Zeitschr. f. Chem.* [2] v. 110).

Pentabromobenzoic acid, $C^7HCl^5O^2 = C^6Cl^5.CO^2H$, is formed by the long-continued action of bromine and water on tribromobenzoic acid at temperatures above 200°; but a considerable portion of it is at the same time resolved into carbon dioxide and pentabromobenzene. The remainder treated with ammonia yields an ammonium salt which may be purified by crystallisation.

Pentabromobenzoic acid has the aspect of sublimed benzoic acid. It is nearly insoluble in boiling water; crystallises from dilute alcohol in thin laminæ or long broad needles; from boiling benzene, in which it is but slightly soluble, it crystallises on cooling in thick, larger needles; melts at 234°-235°, which is also the melting point of tribromobenzoic acid. Heated with a strong solution of sodium acetate to 149°-150° in a sealed tube, it forms an acid which crystallises in needles and turns iron salts blue, doubtless tetrabromosalicylic acid. At a higher temperature carbon dioxide is evolved, in consequence of the further decomposition of this acid.

The metallic *pentabromobenzoates* are all sparingly soluble. The ammonium salt $C^7Br^5(NH^4)O^2$ forms shining laminæ very much like leucine; the potassium and sodium salts also crystallise in flat prisms. The calcium salt $(C^7Br^5O^2)^2Ca.6H^2O$ crystallises from dilute alcohol in scales having a strong lustre (Reinecke, *loc. cit.*).

Chlorobenzoic Acids.

Monochlorobenzoic acid, C^7H^5ClO, is known in the three modifications of ortho- (1 : 2), meta- (1 : 3), and para- (1 : 4).

Orthochlorobenzoic acid, $C^6H^4Cl.CO^2H$, is the modification which Limpricht a. von Uslar obtained by the action of water or alkalis on chlorobenzoyl chloride, $C^6H^4Cl.COCl$ (i. 566). It is also produced by the action of chlorine or hypochlorous acid on benzoic acid (i. 555); of hydrochloric acid on chloro-hippuric acid (Otto, *Jahresb.* 1862, p. 255); of hydrochloric acid on diazobenzo-amidobenzoic acid (Griess). Lastly it is produced by the oxidising action of chromic acid on orthochlorotoluene, $C^6H^4Cl.CH^3$ (Wroblewsky, p. 281). It forms a crystalline mass, slightly soluble in water, easily in alcohol, subliming in crystals, and melting at 151° (Wroblewsky); at 152·5°, not under water (Beilstein a. Schlun, *Jahresb.* 1865, p. 330). By fusion with potassium hydrate it is converted into oxybenzoic acid (Dembey, *Ann. Ch. Pharm.* cxlviii. 221). Its calcium salt, $(C^7H^4ClO^2)Ca.3H^2O$, crystallises well, and dissolves in 82·7 pts. water at 12°.

Metachlorobenzoic or *Chlorosalylic acid*, $C^6H^3ClH.CO^2H$, discovered by Chiozza, and formerly called *parachlorobenzoic acid* (i. 555), is prepared by distilling 1 mol. of salicylic (meta-oxybenzoic) acid, or better of its sodium salt, with 2 mol. phosphorus pentachloride, whereby chlorosalyl chloride, $C^7H^4OCl^2$, is obtained, together with salicyl chloride, $C^7H^5O^2Cl$, and chlorosalyl trichloride, $C^7H^4Cl^4$; rectifying the distillate; and decomposing the portion which distils above 240° and consists mainly of chorosalyl chloride, $C^7H^4ClO.Cl$, with boiling water. The chlorosalylic acid thus obtained may be freed from salicylic acid by once recrystallising it from water (Kolbe a. Lautemann, *Ann. Ch. Pharm.* cxv. 157; *Jahresb.* 1860, p. 288).

Chlorosalylic acid is a crystalline mass composed of white silky needles, melting at 140° (Kolbe a. Lautemann); at 137°, and likewise under water (Beilstein a. Schlun). Dissolves in 881 pts. water at 0°. Like the ortho-acid, it gives with ferric chloride a yellow precipitate, but no violet coloration. It is not decomposed by boiling potash-ley, but is converted into salicylic acid by melting with potassium hydrate. In hot aqueous solution it is easily reduced to benzoic acid[*] by sodium-amalgam, whereas orthochlorobenzoic acid is scarcely affected by that reagent (Kolbe a. Lautemann). Its calcium salt, $(C^7H^4ClO^2)^2Ca.2H^2O$, is very soluble in water (Beilstein a. Schlun). The *ethylic ether*, $C^7H^4ClO^2.C^2H^5$, obtained by treating with alcohol the product of the action of phosphorus pentachloride on salicylic acid (i. 555), is a colourless fragrant liquid, insoluble in water, and boiling at 238°–242° (Kekulé, *Rép. Chim. pure*, 1861, p. 308).

Parachlorobenzoic or *Chlorodracylic* acid, $C^6H^2ClH^2.CO^2H$, is produced: 1. By heating diazo-amidodracylic acid (isomeric with diazo-amidobenzoic acid, iv. 292) with hydrochloric acid (Wilbrand a. Beilstein, *Ann. Ch. Pharm.* cxxviii. 257).—2. By oxidising mono-chlorobenzene with a mixture of dilute sulphuric acid and manganese dioxide. Part of the chlorobenzene then suffers complete decomposition, yielding formic acid, amongst other products, and the formic acid, together with free oxygen, converts the rest of the chlorobenzene into chlorodracylic acid:

$$C^6H^5Cl + H.CO^2H + O = C^6H^4Cl.CO^2H + H^2O.$$

The chlorodracylic acid, the greater part of which remains mixed with undecomposed chlorobenzene, may be extracted therefrom by soda-ley, precipitated by sulphuric acid, and purified by converting it into a barium salt, and decomposing this salt with hydrochloric acid (Carl Müller, *Zeitschr. f. Chem.* [2] v. 137).

Chlorodracylic acid is easily soluble in alcohol and ether, sparingly in water, 1 pt. of the acid requiring for solution 5,288 pts. water. It melts at 235°, and sublimes in fine-needle-shaped prisms and in laminæ (Müller); melts at 236°–237°, and sublimes in scales, but not in needles like the two preceding modifications (Beilstein a. Schlun). Its barium salt, $(C^7H^4ClO^2)Ba.4H^2O$, crystallises in prisms and laminæ; the calcium salt has the composition $(C^7H^4ClO^2)Ca.3H^2O$.

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[*] The benzoic acid thus obtained is impure, and was for some time regarded as a distinct acid, called by Kolbe a. Lautemann *salylic acid*; but Beilstein a. Schlun have shown that, when purified by distillation in aqueous vapour, it exhibits all the properties of ordinary benzoic acid.

Dichlorobenzoic Acid. $C^7H^4Cl^2O^2 = C^6H^3Cl^2.CO^2H$ (Otto, *Ann. Ch. Pharm.* cxxii. 129; cxxiii. 216; *Jahresb.* 1862, 253, 255. Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2] iv. 661; v. 180, 526; *Ann. Ch. Pharm.* clii. 224).—Produced: 1. By distilling chlorobenzene-sulphuric acid with phosphorus pentachloride, whereby chlorobenzoyl chloride, $C^7H^4ClO.Cl$, is produced, and decomposing this chloride with potash.—2. By prolonged boiling of dichlorhippuric acid with strong hydrochloric acid (Otto).—3. By oxidising dichlorotoluene with chromic acid:

$$C^6H^3Cl^2.CH^3 + O^3 = C^6H^3Cl^2.CO^2H + H^2O.$$

4. By heating dichlorobenzene trichloride with water in a sealed tube:

$$C^6H^3Cl^2.CCl^3 + 2H^2O = C^6H^3Cl^2.CO^2H + 3HCl.$$

5. By boiling benzoic acid with solution of chloride of lime, whereby calcium monochlorobenzoate appears to be formed in the first instance:

$$2C^7H^6O^2 + 2CaCl^2O = (C^7H^4ClO^2)^2Ca + CaCl^2 + 2H^2O.$$

The chloride of lime solution acts very quickly on the free acid, but scarcely at all on the calcium salt; hence, as soon as the liquid becomes neutral, it is necessary to precipitate the monochlorinated acid by addition of hydrochloric acid, filter off the liquid, and again boil the crude acid with chloride of lime solution; the reaction then goes on further, and the calcium salt of dichlorobenzoic acid is produced:

$$2C^7H^5ClO^2 + 2CaCl^2O = (C^7H^3Cl^2O^2)^2Ca + CaCl^2 + 2H^2O.$$

The liquid is again acidulated, and the treatment with chloride of lime repeated a third, and sometimes even a fourth time; if, however, the treatment be too much prolonged, part of the product is converted into trichlorobenzoic acid. The crude dichlorinated acid is then combined with baryta, the barium salt purified by recrystallisation (1 pt. dissolves in 100 pts. of water), and the acid precipitated from it by hydrochloric acid (Beilstein a. Kuhlberg).

Dichlorobenzoic acid exhibits the same properties, by whichever of the preceding processes it may be prepared (Beilstein, *Zeitschr. f. Chem.* [2] v. 180). It is sparingly soluble in cold, more freely in hot water, easily soluble in alcohol, crystallises from water in slender needles, melts at 201°,[*] and distils without decomposition. Fuming nitric acid converts it into monochloronitrobenzoic acid (Beilstein a. Kuhlberg). By sodium-amalgam it is reduced to benzoic acid (Otto).

The barium salt $(C^7H^3Cl^2O^2)^2Ba.4H^2O$ crystallises in slender shining needles, slightly soluble in water. The calcium salt $(C^7H^3Cl^2O^2)^2Ca.3H^2O$ crystallises in shining scales. The ethylic ether, a fragrant liquid, boiling at 262°–263°, is obtained by heating dichlorotoluene-trichloride with absolute alcohol to 180°:

$$C^6H^3Cl^2.CCl^3 + 4C^2H^6O = C^6H^3Cl^2.CO^2C^2H^5 + 3C^2H^5Cl + 2H^2O.$$

Dichlorobenzoyl chloride, $C^7H^3Cl^2O.Cl$, produced by the action of phosphorus pentachloride on dichlorobenzoic acid (B. and K.), or on chlorobenzene-sulphuric acid (Otto), is a liquid boiling without decomposition at 242° (B. and K.).

Dichlorobenzamide, $C^7H^3Cl^2O.NH^2$, is obtained by treating the chloride with ammonia, or directly by heating dichlorotoluene trichloride with an equivalent quantity of ammonia to 200°:

$$C^6H^3Cl^2.CCl^3 + 4NH^3 + H^2O = C^6H^3Cl^2.CONH^2 + 3NH^4Cl.$$

It forms beautiful silky, yellowish needles, melting at 133°, volatilising with vapour of water, more soluble in boiling than in cold water. Heated with excess of ammonia to 200°, it decomposes with elimination of chlorine (B. and K.).

Trichlorobenzoic Acid. $C^7H^3Cl^3O^2 = C^6H^2Cl^3.CO^2H$ (Janasch, *Zeitschr. f. Chem.* [2] iii. 404. Beilstein a. Kuhlberg, *ibid.* iv. 663; v. 526; *Ann. Ch. Pharm.* clii. 224).—Produced: 1. By oxidising trichlorotoluene with chromic acid mixture:

$$C^6H^2Cl^3.CH^3 + O^3 = C^6H^2Cl^3.CO^2H + H^2O;$$

but the conversion is very slow.—2. By heating trichlorotoluene-trichloride with water to 260° in sealed tubes:

$$C^6H^2Cl^3.CCl^3 + 2H^2O = C^6H^2Cl^3.CO^2H + 3HCl.$$

The reaction takes place quickly, and almost without formation of secondary products, the trichlorinated acid often crystallising in the tubes. It is extracted by repeated boiling with ammonia, and precipitated by hydrochloric acid (B. and

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[*] Otto observed lower melting points for the acid obtained by the first and second processes; but his descriptions of the salts agree in all essential particulars with those given by Beilstein a. Kuhlberg.

K.).—3. By boiling the dichlorinated acid with strong solution of chloride of lime, precipitating the neutral solution with hydrochloric acid, and repeating the same treatment on the precipitated acid till the conversion is nearly complete. To purify the product from remains of the dichlorinated acid, it is converted into the ethylic ether, which, being solid, may be freed from adhering dichlorinated ether by pressure and recrystallisation from alcohol; when decomposed by strong potash-solution, it yields the pure acid. The three modes of preparation yield the acid with exactly the same properties; the second is the most expeditious (B. and K.).

Trichlorobenzoic acid crystallises in very slender needles melting at 163° (B. and K.); 160° (Janasch); scarcely soluble in cold, sparingly in boiling water, freely in alcohol and ether. The *ammonium salt* $C^7H^2Cl^3O^2(NH^4).H^2O$ is crystalline and very slightly soluble in cold water. The *barium salt* $(C^7H^2Cl^3O^2)^2Ba.7H^2O$ crystallises in slender silky needles, moderately soluble in hot water. The *calcium salt* $(C^7H^2Cl^3O^2)^2Ca.2H^2O$ forms small needles more soluble than the barium salt. The *strontium salt* $(C^7H^2Cl^3O^2)^2Sr.4H^2O$ is easily soluble in boiling water, and crystallises on cooling in small white needles. The *magnesium salt* is extremely soluble; the *zinc salt* forms slender needles; the *lead salt* is moderately soluble in hot water; the *copper salt* is a green insoluble precipitate. The *ethylic ether* $C^7H^2Cl^3O^2.C^2H^5$ crystallises from alcohol in long flat white needles, melts at 65°, and has a faint fruity odour.

Trichlorobenzoic chloride, $C^6H^2Cl^3.COCl$, boils almost without decomposition at 272°, melts at about 41°, and is extremely soluble in benzol, ether, and carbon bisulphide.

Trichlorobenzamide, $C^6H^2Cl^3.CONH^2$, produced by the action of ammonia on the chloride, is very sparingly soluble in water even at the boiling heat, easily soluble in alcohol, and crystallises from benzol in slender white needles melting at 167·5° (Beilstein a. Kuhlberg).

Tetrachlorobenzoic acid (para), $C^7H^2Cl^4O^2 = C^6HCl^4.CO^2H$, is prepared by heating tetrachlorobenzotrichloride, $C^6HCl^4.CCl^3$, with water to 270°–280°. It melts at 187°. Its barium salt crystallises in slender needles (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2] v. 75, 528).

Iodobenzoic Acids.

Only the monoiodated acid is known, in two modifications.

Ortho-iodobenzoic acid, $C^6H^4I.CO^2H$, is produced by the action of hydriodic acid or of iodine on diazobenzo-amidobenzoic acid (Griess, *Jahresb.* 1859, p. 466; 1861, p. 411. Cunze a. Hübner, *ibid.* 1865, p. 331); also by the action of iodic acid on benzoic acid (Peltzer, *Ann. Ch. Pharm.* cxxxvi. 194); and by oxidising ortho-iodotoluene (p. 284) with chromic acid mixture (Körner, *Zeitschr. f. Chem.* [2] v. 637). It crystallises in needles slightly soluble in water, easily soluble in alcohol, subliming without decomposition (Griess), melting at 187° (Cunze a. Hübner). According to Körner, it melts at 172·5°, and is converted by fusion with potash into oxybenzoic acid. Converted by ammonia into amidobenzoic acid; by strong nitric acid into nitro-iodobenzoic acid.

Barium iodobenzoate, $(C^7H^4IO^2)^2Ba.2H^2O$, forms needles soluble in alcohol; the *calcium salt* $(C^7H^4IO^2)^2Ca$ crystallises in hard anhydrous nodules and in shining scales containing 1 mol. of water. The *magnesium salt* $(C^7H^4IO^2)^2Mg.2H^2O$ forms easily soluble nodules; the *sodium salt* $C^7H^4IO^2Na.H^2O$ four-sided tables (Cunze a. Hübner). The *silver salt* $C^7H^4IO^2Ag$ is white, insoluble in water and in alcohol (Griess). The *ethylic ether* $C^7H^4IO^2.C^2H^5$ is a liquid, insoluble in water, not converted into idobenzamide by contact with ammonia.

Para-iodobenzoic acid, $C^6H^2IH^2.CO^2H$, is formed by oxidising para-iodotoluene, $C^6H^2IH^2.CH^3$, with chromic acid mixture. When purified by conversion into a sodium salt, precipitation by hydrochloric acid, and recrystallisation from alcohol, it forms nacreous scales, nearly insoluble in boiling water, easily soluble in boiling alcohol; does not melt at 250°, but begins to sublime at 230° in white laminæ having a strong lustre. Its sodium salt crystallises in long transparent needles. The acid is converted by melting potash into a crystalline acid, possessing the appearance and properties of para-oxybenzoic acid (W. Körner, *Zeitschr. f. Chem.* [2] iv. 327).

Nitrobenzoic Acids.

Mononitrobenzoic acid, $C^6H^4(NO^2).CO^2H$, is known with certainty only in two modifications, ortho- and para-.

Orthonitrobenzoic acid is produced by the action of fuming nitric acid, or of a mixture of potassium nitrate and sulphuric acid on benzoic acid, and by several other processes already mentioned (i. 555); also, together with nitrodracylic acid, in the oxidation of toluene by fuming nitric acid (Reichenbach a. Beilstein, *Ann. Ch. Pharm.* cxxxii. 137). This acid melts under water below 100°, but in the dry state, according to Mills (*Chem. Soc. J.* [2] iv. 363), at 128°. According to A. Naumann (*Jahresb.* 1865, p. 333), the acid separated from its ethylic ether by potash melts at 141°–142°. Its barium salt, $[C^7H^4(NO^2)O^2]^2Ba.4H^2O$, crystallises in thin flattened needles, mostly in radiate groups. It dissolves (reckoned as anhydrous) in 425 to 475 pts. water at 8°–10°; the acid separated from this salt after five recrystallisations, and heated for a few minutes to 137°, yielded a barium salt soluble in 328·5 pts. water (Mills). The acid treated with tin and hydrochloric acid is reduced to amidobenzoic acid, which forms a double salt with stannous chloride, $C^7H^5(NH^2)O^2.HCl.SnCl^2$; with zinc and hydrochloric acid, it likewise yields amidobenzoic acid; with zinc and caustic soda, an intermediate product appears to be formed (Wilbrand a. Beilstein, *Jahresb.* 1863, p. 342). With alcoholic potash it yields azoxybenzoic acid and aldehyde (Griess, *Ann. Ch. Pharm.* cxxxi. 92):

$$\underset{\substack{\text{Nitrobenzoic}\\\text{acid.}}}{2C^7H^5(NO^2)O^2} + \underset{\text{Alcohol.}}{3C^2H^6O} = \underset{\substack{\text{Azoxybenzoic}\\\text{acid.}}}{C^{14}H^{10}N^2O^5} + \underset{\text{Aldehyde.}}{3C^2H^4O} + 3H^2O.$$

Sodium nitrobenzoate strongly heated with iodine monochloride yields, together with sodium chloride and free iodine, an oily mixture of mono-iodonitrobenzene, $C^6H^4(NO^2)I$, with a small quantity of a crystalline body, probably di-iodonitrobenzene, $C^6H^3(NO^4)I^2$ (Schützenberger a. Sengenwald, *Jahresb.* 1862, p. 251). The *ethylic ether* heated with bromine to 170°–200° is resolved into nitrobenzoic acid (melting at 141°–142°) and ethylene bromide, sometimes mixed with a yellowish-white nitrogenous acid insoluble in ether, cold alcohol, and water:

$$C^7H^4(NO^2)O^2.C^2H^5 + Br^2 = C^7H^5(NO^2)O^2 + C^2H^4Br^2$$

(A. Naumann, *Ann. Ch. Pharm.* cxxxiii. 199).

Paranitrobenzoic or *Nitrodracylic acid.* $C^6H^2(NO^2)H^2.CO^2H$.—Produced, together with the ortho-acid, by the action of fuming nitric acid on toluene (iv. 60), part of the toluene being oxidised to benzoic acid, which is then converted into nitrobenzoic acid, while the greater portion of the toluene is transformed into nitrotoluene, which is then oxidised to nitrodracylic acid. Crystallised nitrotoluene is completely converted into nitrodracylic acid by oxidation with chromic acid (Körner, *Zeitschr. f. Chem.* [2] v. 636; Rosenstiehl, *ibid.* 701). The oxidation of nitrotoluene with chromic acid affords a very convenient mode of obtaining pure nitrodracylic acid. For this purpose a mixture of 10 pts. nitrotoluene, 40 pts. potassium dichromate, and 55 pts. sulphuric acid diluted with twice its volume of water, is heated in a flask provided with a condensing tube, and the nitrated acid is extracted from the filtered residue by sodium carbonate. By precipitating the alkaline solution with hydrochloric acid, and once recrystallising the precipitate, nitrodracylic acid is obtained in the pure state (Beilstein a. Geitner, *Ann. Ch. Pharm.* cxxxix. 331). Nitrodracylic acid is likewise obtained (together with nitrobenzoïn), by treating deoxybenzoïn with nitric acid (Zinin, *Ann. Ch. Pharm.* cxxvi. 218; *Zeitschr. f. Chem.* [2] iv. 563).

Nitrodracylic acid melts at 236°–240°, not under boiling water; it is slightly soluble in cold water (1 pt. in 1327 pts. at 16°). Its *zinc salt*, $[C^7H^4(NO^2)O^2]^2Zn.2H^2O$, dissolves (anhydr.) in 152·7 pts. of water at 170° (Mills, *loc. cit.*). The *calcium salt* $[C^6H^4(NO^2)O^2]^2Ca.8H^2O$ forms large tabular efflorescent crystals, whereas the corresponding salt of orthonitrobenzoic acid contains only 2 mol. water, and crystallises in slender needles. *Sodium nitrodracylate*, $C^7H^4(NO^2)O^2Na.3H^2O$, contains the same proportion of water as the nitrobenzoate; the crystals of both salts are triclinic prisms terminated by oblique faces; but those of the nitrodracylate are cleavable parallel to one of the end-faces, whereas those of the nitrobenzoate do not exhibit this direction of cleavage (Billinger, *Jahresb.* 1865, p. 334).

The following comparison (p. 315) of the crystalline forms and solubilities of certain salts of ortho- and para-nitrobenzoic acid is given by Sokoloff (*Jahresb.* 1864, p. 343).

Mill describes two other modifications (γ and δ), obtained by treating benzoic acid with a mixture of nitric and sulphuric acids, the latter remaining in the mother-liquor after the former has crystallised out: they are both, however, very much like the ortho-acid, differing from it chiefly by a somewhat higher melting-point (135°–142°): moreover, the process by which they are formed is almost the same as that by which Gerland obtained the ordinary ortho-acid (i. 555).

Dinitrobenzoic acid is described in vol. i. p. 557.

Forms and Solubilities of Ortho- and Para-nitrobenzoic Acids [$NO^2 = X$].

	Formula	Crystalline Form	1 pt. salt dissolves in pts. of water	
			at 100°	at ordinary temp.
o. Potassium salt . . .	$C^7H^4XO^2K.H^2O$	Needles	0·5	7
p. Potassium salt . . .	$C^7H^4XO^2K.2H^2O$	Rhomb. tables	0·5	3
o. Calcium salt	$(C^7H^4XO^2)^2Ca.H^2O$	Laminæ	18	30
p. Calcium salt	$(C^7H^4XO^2)^2Ca$	Laminæ	12	32
o. Barium salt	$(C^7H^4XO^2)^2Ba.2H^2O$	Needle	19	265
p. Barium salt	$(C^7H^4XO^2)^2Ba.2H^2O$	Thin prisms	8	250
o. Zinc salt	$(C^7H^4XO^2)^2Zn.2H^2O$	Needles	13	63
p. Zinc salt	$(C^7H^4XO^2)^2Zn.H^2O$	Laminæ	80	135

Nitrobromobenzoic Acid. $C^7H^4Br(NO^2)O^2 = C^6H^3Br(NO^2).CO^2H$ (Hübner a. Ohly, *Zeitschr. f. Chem.* [2] i. 547; ii. 241; *Ann. Ch. Pharm.* cxliii. 230).—Two modifications of this acid (α and β) are formed by the action of fuming nitric acid on bromobenzoic acid. If when the first violent action is over, the mixture be gently warmed till the whole of the bromobenzoic acid is dissolved, and then mixed with cold water, the less soluble modification (α-bromonitrobenzoic acid) separates out, while the more soluble (β-bromonitrobenzoic acid) remains in the liquid, and may be obtained in the solid state by evaporation. The latter when purified by recrystallisation or sublimation forms, according to O. Philipp, monoclinic combinations $(\infty P\infty) . \infty P . - P . oP$, having the angle $oP : (\infty P\infty) = 90° 23'$; $(\infty P\infty) : \infty P = 140° 11'$; no distinct cleavage. Melting point, 140°–141°. The *ammonium salt* forms yellowish laminæ; the *potassium salt* $C^7H^3Br(NO^2)K.2H^2O$, transparent shining needles easily soluble in water, sparingly in alcohol. The *sodium salt* $2C^7H^3Br(NO^2)Na.5H^2O$ crystallises from a highly concentrated aqueous solution in yellowish pointed prisms gradually changing to four-sided tables; from the alcoholic solution also in tables. The *silver salt* is obtained by precipitation in anhydrous silky needles. The *barium salt* $[C^7H^3Br(NO^2)O^2]^2Ba$ forms white needles; the *calcium salt* separates from strong solutions in small white nodules containing $[C^7H^3Br(NO^2)O^2]^2Ca.2H^2O$, and the mother-liquor deposits asbestos-like needles of the anhydrous salt. The *magnesium salt* $[C^7H^3Br(NO^2)O^2]^2Mg.4H^2O$ forms yellowish elongated, apparently rhombic tables. The *lead salt* forms indistinct white crystals; the *copper salt* is obtained by precipitation in greenish crystals: both these salts are anhydrous. The *ethylic ether* $C^7H^3Br(NO^2)O^2.C^2H^5$ crystallises from alcohol in shining monoclinic prisms exhibiting the combination $(\infty P\infty) . \infty P . \pm P\infty . oP$, with the clinopinacoïd predominant, and the angle $\infty P : \infty P$ (clinod.) $= 115° 8'$; cleaving distinctly parallel to oP, less distinctly parallel to $(\infty P\infty)$. The crystals melt at 55°, and are easily soluble in ether.

α-Nitrobromobenzoic acid appears to be formed in greatest quantity when the process is so conducted as not to allow the mixture to get very hot, and remains undissolved when the product is treated with cold water. It is purified by repeated boiling with water, till the residue no longer melts under water, and crystallises from ether in large colourless shining octohedrons which are monoclinic combinations of $+P$ and $-P$ with $(P\infty)$ very subordinate. Melting point, 246°–248°. The *sodium salt* crystallises sometimes in small nodules, sometimes in rhombic tables; the *silver salt* in white, anhydrous, very soluble needles decomposing at 110°. The *barium salt* $[C^7H^3Br(NO^2)O^2]^2Ba.4H^2O$, and the *calcium salt*, form easily soluble laminæ; the *magnesium salt*, which is soluble even in cold water, forms long needles containing $6H^2O$; the *lead salt* forms small needles soluble in hot water. The *ethylic ether* crystallises from ether in colourless monoclinic prisms $\infty P . \infty P\infty . -P\infty . oP$, elongated in the direction of the prismatic axis, cleaving very distinctly parallel to oP, and having the angle $\infty P : \infty P$ (clinod.) $= 47° 5'$. They melt at 80°, and dissolve very easily in alcohol and in ether.

The two varieties of nitrobromobenzoic acid just described differ also in their behaviour with reducing agents (p. 317).

Paranitrobromobenzoic or *Nitrobromodracylic acid*, $C^7H^4Br(NO^2)O^2$, produced by the action of fuming nitric acid on bromodracylic acid, forms a granulo-crystalline mass melting at 199°, subliming in slender needles, sparingly soluble in cold, more easily

Chloramidobenzoic Acid, $C^7H^4Cl(NH^2)O^2$, produced by the action of ammonium sulphide on nitrochlorobenzoic acid, crystallises in light yellow nodules slightly soluble in water, easily in alcohol and ether; it volatilises with partial decomposition and sublimes in tufts of needles which melt at 145°–148°, turning brown at the same time. It is a stronger acid than amidobenzoic acid, and forms brown precipitates with solutions of those metals which are precipitable from acid solution by hydrogen sulphide, also with ferrous salts, white with uranium salts. Its potassium, sodium, and magnesium salts, also the slightly soluble barium salt, crystallise in nodules, the potassium salt with $2H^2O$, the barium salt with $5H^2O$, the calcium salt with $3H^2O$.

Chloramidobenzoic acid dissolved in alcohol and treated with a current of nitrous acid gas is converted into diazochlorobenzo-amidochlorobenzoic acid, $C^{14}H^9Cl^2N^3O^4$, which forms a yellowish-red crystalline powder. On heating chloramidobenzoic acid with dilute sulphuric acid, and adding barium carbonate to the solution, warty crystals are obtained consisting of the barium salt of sulphamidochlorobenzoic acid, $C^7H^3Cl(NH^2).SO^3H$ (Cunze a. Hübner, *Ann. Ch. Pharm.* cxxxv. 106).

Hemicyanamidobenzoic Acid. $C^7H^{6\frac{1}{2}}(CN)^{\frac{1}{2}}NO^2$ or $C^{14}H^{13}(CN)N^2O^4$ (Griess, *Zeitschr. f. Chem.* [2] iii. 533; iv. 389, 650).—This acid, consisting of a double molecule of amidobenzoic acid having 1 at. H replaced by cyanogen, is contained, together with neutral cyanethyl amidobenzoate, in the alcoholic mother-liquor from which amidobenzoic cyanide (p. 317) has been deposited. The two compounds separate out together, after standing for several weeks, in the form of a white crystalline precipitate, and may be separated by treatment with hot water, in which the hemicyanamidobenzoic acid dissolves more readily than the neutral compound, and is deposited on cooling in white needles. For further purification it is dissolved in hot dilute hydrochloric acid; and the solution, after decolorisation with animal charcoal, is mixed with a quantity of ammonia sufficient to redissolve the precipitate, and afterwards with acetic acid. The hemicyanamidobenzoic acid then separates as an amorphous mass, which gradually becomes crystalline. It unites, like amidobenzoic acid, both with other acids and with bases. The *barium salt* $(C^{15}H^{12}N^3O^4)^2Ba$ crystallises in white needles moderately soluble in hot water. The *hydrochloride* $C^{15}H^{13}N^3O^4.HCl$ forms granular or needle-shaped crystals, easily soluble in water, very slightly soluble in hydrochloric acid. The *platinochloride* $2(C^{15}H^{13}N^3O^4HCl).PtCl^4$ crystallises in slightly soluble nodules.

Cyanethyl Amidobenzoate. $C^{20}H^{30}N^4O^9 = 2C^7H^5(C^2H^5CN)NO^2.5H^2O$.—This compound, which may also be regarded as $2[C^7H^4(C^2H^5)(NH^2)O^2.CHNO].3H^2O$, that is, as ethylamidobenzoic cyanate with 3 mol. water, forms, after recrystallisation from boiling water, needle-shaped crystals easily soluble in alcohol and ether. Its solution in dilute acids or alkalis is decomposed by heat, with separation of an acid having the composition $C^8H^8N^2O^3$:

$$C^{20}H^{30}N^4O^9 = 2C^8H^8N^2O^3 + 2C^2H^6O + H^2O.$$

This acid, called uramidobenzoic acid by Griess, oxybenzuramic acid by Menschutkin (*Zeitschr. f. Chem.* [2] iv. 275), who obtained it by adding potassium cyanate to a boiling saturated solution of amidobenzoic sulphate:

$$(C^7H^7NO^2)^2.H^2SO^4 + 2KCNO = 2C^8H^8N^2O^3 + K^2SO^4,$$

is also prepared by fusing amidobenzoic acid with urea at a gentle heat, dissolving the mass in a large quantity of hot water, and supersaturating with hydrochloric acid (Griess, *Zeitschr. f. Chem.* [2] v. 312):

$$C^7H^7NO^2 + CH^4N^2O = NH^3 + C^8H^8N^2O^3.$$

It crystallises in small prisms containing 1 mol. water, which they give off at about 100°; dissolves very sparingly in boiling water, is slightly more soluble in alcohol, almost insoluble in ether. Its salts are all soluble in water and difficult to crystallise (Menschutkin). Heated to about 200°, it is resolved into urea and an acid, $C^{15}H^{12}N^2O^5$, homologous with azoxybenzoic acid, and resembling it in most of its properties:

$$2C^8H^8N^2O^3 = CH^4N^2O + C^{15}H^{12}N^2O^5.$$

The same decomposition takes place on repeatedly evaporating the aqueous solution of barium uramidobenzoate. From the solution of the resulting barium salt the acid $C^{15}H^{12}N^2O^5$ is separated by hydrochloric acid in microscopic needles. It is nearly insoluble in water, alcohol, and ether. Its ammoniacal solution forms white precipitates with barium chloride and silver nitrate (Griess).

Uramidobenzoic acid is converted by fuming nitric acid into a nitrated acid, $C^8H^6(NO^2)^2N^2O^3$, which is easily soluble in alcohol and especially in ether; dissolves also without decomposition in a large quantity of moderately warm water, but is decomposed on boiling the solution, with evolution of gas, and formation of two isomeric acids, $C^7H^6N^2O^4$, one (α) very sparingly soluble in boiling water and separating out almost as soon as it is formed, while the other (β) remains in solution. The α-acid crystallises from boiling alcohol in tufts of yellowish-red shining laminæ, subliming at a moderate heat in rhombic laminæ, melting and afterwards decomposing at a higher temperature. The more soluble β-acid, purified by several recrystallisations from boiling water, forms thick yellow needles or prisms, sparingly soluble in cold water, easily soluble in alcohol and ether, fusing when heated and subsequently decomposing, with detonation and emission of yellow fumes. The *α-barium salt*, $(C^7H^5N^2O^4)^2Ba.2H^2O$, forms yellowish-red prisms which are very slightly soluble in water, and do not give off the whole of their crystallisation-water till heated to 190°. The *β-barium salt*, $(C^7H^5N^2O^4)^2Ba.7H^2O$, crystallises in needles, very soluble even in cold water. Both these acids are reduced by tin and hydrochloric acid, yielding amidated acids having the composition of diamidobenzoic acid, $C^7H^8N^2O^2$, both being very soluble in hot water and separating for the most part on cooling, the α-acid in yellowish laminæ, the β-acid in needles, both quickly assuming a reddish colour on exposure to the air. The hydrochlorides of these amidated acids are quickly reduced by sodium nitrite to the corresponding azo-acids $C^7H^5N^3O^7$, crystallising in hydrated needles which give off their water of crystallisation at 100° (Griess, *Zeitschr. f. Chem.* [2] v. 699).

Meta-amidobenzoic, Amidosalylic, or Anthranilic Acid. $C^7H^5(NH^2)O^2$.—This acid, originally obtained by boiling indigo with potash (see Phenyl-carbamic Acid, i. 751), has lately been formed by the action of sodium-amalgam on bromamidobenzoic acid (Hübner a. Petermann, *Zeitschr. f. Chem.* [2] iv. 205, 546; *Ann. Ch. Pharm.* cxlix. 129). The bromamidobenzoic acid (p. 317) having been shaken up for a considerable time with sodium-amalgam, the acidulated solution was precipitated with cupric acetate, the resulting cupric salt decomposed with hydrogen sulphide, the liberated amidobenzoic acid saturated with sulphuric acid, and the amidobenzoic sulphate crystallised out. To obtain the free amidobenzoic acid, the sulphate was neutralised with barium carbonate, the resulting barium salt decomposed with cupric acetate, and the precipitated copper salt decomposed with hydrogen sulphide and purified by recrystallisation.

The amidobenzoic acid thus prepared, whether from α- or β-bromamidobenzoic acid, forms long shining colourless needles, exactly resembling those of anthranilic acid from indigo, and melting at 144°, which is also the melting point of anthranilic acid (not 132°, as stated in vol. i.). Moreover, when treated with nitrous acid, not in excess, it is converted (like anthranilic acid) into meta-oxybenzoic or salicylic acid, distinguished from ortho- and para-oxybenzoic acids by the characteristic blue-red colour which it gives with ferric salts.

The amidobenzoic acid prepared as above is therefore meta-amidobenzoic or amidosalylic acid. This result is intelligible if we suppose that in bromamidobenzoic acid the radicles CO^2H, Br, and NH^2 occupy the places 1 : 2 : 3, thus, $C^6H^3(NH^2)Br.CO^2H$; so that when the bromine is replaced by hydrogen, the molecule $C^6H^3(NH^2)H.CO^2H$ is formed, in which the CO^2H and NH^2 occupy the positions 1, 3.

The salts of amidosalylic acid prepared from bromamidobenzoic acid (α or β) also exactly resemble those of anthranilic acid from indigo. The *barium salt* $(C^7H^6NO^2)^2Ba$ crystallises easily in shining flat needles; the ortho-amidobenzoate, on the other hand, forms needles which are not flattened and contain $8H^2O$. The *copper salt* $(C^7H^6NO^2)^2Cu$ forms a green precipitate much lighter and more bluish than the ortho-amidobenzoate. The *silver salt* $C^7H^6NO^2Ag$ forms slender needles which may be recrystallised without decomposition, and have when dry the aspect of metallic silver; the ortho-amidobenzoate is much less stable. The *lead salt* $(C^7H^6NO^2)^2Pb$ is either a dense white precipitate, or crystallises from aqueous or alcoholic solution in shining silver-white needles, which turn yellowish when exposed to light. *Amidosalylic sulphate*, $(C^7H^7NO^2)^2.H^2SO^4$, crystallises from water in thick obliquely truncated prisms containing $2H^2O$, which give off their water at 125°, and melt at 188°; and from dilute alcohol, in long thin groups of needles containing 1 mol. of water (Hübner a. Petermann).

The action of *cyanogen* on anthranilic acid is very different from that which it exerts on ortho-amidobenzoic acid. When cyanogen gas is passed into an alcoholic solution of anthranilic acid, little or no precipitation of an additive product $(C^7H^7NO^2.Cy^2)$ takes place; but on leaving the saturated solution to itself for about a week, the anthranilic acid is almost wholly converted into the ethylic ether of cyananthranilic acid, $C^{10}H^{10}N^2O^2 = C^7H^5(CN)NO^2.C^2H^5$, while two other compounds, an acid and an indifferent substance (not isomeric with any of the bodies obtained in like manner from amidobenzoic acid), are formed at the same time in small quantity. To separate the cyananthranilic ether, the alcoholic solution is evaporated at a gentle heat, and the crystalline residue is washed with dilute ammonium carbonate to remove the acid product, and further purified by recrystallisation from alcohol with addition of animal charcoal. It is thus obtained in white needle-shaped crystals, very slightly soluble in boiling water, freely soluble in boiling alcohol and ether. Its formation is represented by the equation:

$$C^7H^7NO^2 + 2CN + C^2H^6O = C^{10}H^{10}N^2O^2 + CHN + H^2O.$$

Cyananthranilic ether dissolves without alteration in cold hydrochloric acid, but on boiling the solution, decomposition takes place, resulting in the formation of alcohol and cyananthranilic acid, $C^8H^6N^2O^2$ or $C^7H^5(CN)NO^2$, isomeric with azodioxindol (see ISATIN), the latter separating out:

$$C^{10}H^{10}N^2O^2 + H^2O = C^2H^6O + C^8H^6N^2O^2.$$

Cyananthranilic acid dissolves very slightly in boiling water, alcohol, and ether, and crystallises in small white brilliant plates melting above 350°; the solutions are neutral to test-paper. The acid dissolves in aqueous caustic alkalis, but is precipitated by carbonic acid: its aqueous or alcoholic solution gives a white precipitate with silver nitrate. Fuming nitric acid converts it into the nitro-compound $C^7H^4(NO^2)(CN)NO^2$, which is reduced by ammonium sulphide, or by tin and hydrochloric acid, to the corresponding amido-compound $C^7H^4(NH^2)(CN)NO^2$, which is basic, and crystallises in slightly yellowish needles difficultly soluble in all neutral liquids. Its compounds with acids generally crystallise well, but are for the most part sparingly soluble.

Cyananthranilic ether digested at 100° in sealed tubes with alcoholic *ammonia* is gradually converted into a base, $C^8H^7N^3O = C^7H^4(CN)(NH^2)NO$, which is almost insoluble in water, slightly soluble in boiling alcohol, and crystallises from the latter in brilliant nacreous plates:

$$C^{10}H^{10}N^2O^2 + NH^3 = C^8H^7N^3O + C^2H^6O.$$

This base is mono-acid. Its nitrate is almost insoluble in water and in alcohol, and separates from very dilute solutions of the base in small white plates on addition of nitric acid. Its platinum salt $2(C^8H^7N^2O.HCl).PtCl^4$ crystallises in thick yellow needles. The base may perhaps be regarded as the creatinine of the benzoic series, standing to anthranilic acid in the same relation as creatinine, $C^4H^7N^3O$, to sarcosine, $C^3H^7NO^2$ (Griess, *Proc. Roy. Soc.* xviii. 91).

PARA-AMIDOBENZOIC or AMIDODRACYLIC ACID, $C^6H^2(NH^2)H^2.CO^2H$, produced by the action of ammonium sulphide or of tin and hydrochloric acid on nitrodracylic acid, has already been described as PARA-OXYBENZAMIC ACID (iv. 343).

Its *barium salt* $(C^7H^6NO^2)^2Ba$ is easily soluble, and crystallises in small shining laminæ. The *copper salt* produced by mixing the solution of the calcium salt with cupric acetate, is a dark-green precipitate insoluble in water, easily soluble in ammonia and in acetic acid; the *lead salt* forms pale yellow crystals having a vitreous lustre. *Amidodracylic sulphate*, $2C^7H^7NO^2.H^2SO^4$, separates from water acidulated with sulphuric acid, in furcate tufts of crystals easily soluble in hot, sparingly in cold water (Geitner a. Beilstein, *Ann. Ch. Pharm.* cxxxix. 1; *Jahresb.* 1866, p. 350).

Dibromamidodracylic acid, $C^7H^3Br^2(NH^2)O^2$, is produced by the action of bromine and water on an acidulated solution of amidodracylic acid, as a flocculent precipitate, which, when freed from admixed tribromaniline by solution in ammonia and precipitation with hydrochloric acid, crystallises from hot alcohol in needles. Its *sodium salt* $C^7H^2Br^2(NH^2)O^2Na.5H^2O$ crystallises in silky needles; the *ammonium salt* in tufts of needles; the *barium salt* $[C^7H^2Br^2(NH^2)O^2]^2Ba.4H^2O$ is slightly soluble in cold water; the *calcium salt* $(C^7H^4Br^2NO^2)^2Ca.6H^2O$ and the *magnesium salt* are easily soluble in water; the *zinc*, *copper*, and *silver salts* are insoluble flocculent precipitates.

Dibromamidodracylic acid is easily reduced by sodium-amalgam to amidodracylic acid. With nitrous acid in hot alcoholic solution it yields dibromodracylic acid, $C^7H^4Br^2O^2$, which sublimes in needles (Geitner a. Beilstein, *Zeitschr. f. Chem.* [2] i. 505).

Diamidobenzoic acid, $C^7H^8N^2O^2 = C^7H^4(NH^2)^2O^2$, is described in vol. iv. p. 294 as DIOXYBENZAMIC ACID.

Azobenzoic Acid. $C^{14}H^{10}N^2O^4$ (Strecker, *Ann. Ch. Pharm.* cxxix. 129).—The sodium salt of this acid is produced by treating a concentrated aqueous solution of sodium nitrobenzoate with sodium-amalgam, the reduction taking place without evolution of hydrogen or formation of ammonia. It is also produced, together with glycocine, by the action of sodium-amalgam on nitrohippuric acid. On mixing the orange-yellow solution of the sodium salt with acetic or dilute sulphuric acid, azobenzoic acid separates as a light yellow gummy precipitate, which becomes pulverulent on boiling the liquid with addition of alcohol. After drying it is light yellow and amorphous; it does not lose weight when heated to 100°–170°, but melts with decomposition at a higher temperature. When dried at 100° it contains $2C^{14}H^{10}N^2O^4.H^2O$. It is but slightly soluble in water, alcohol, and ether, dissolves with yellow colour in strong sulphuric acid, and is precipitated therefrom by water without alteration. Ammonia and the hydrates and carbonates of the alkali-metals dissolve it with lemon-yellow colour; the ammoniacal solution when evaporated leaves an acid ammoniacal salt.

Barium azobenzoate, $2C^{14}H^8N^2O^4Ba.5H^2O$, is a lemon-yellow or orange-yellow granular precipitate, nearly insoluble in water and in alcohol, which gives off four-fifths of its water at 100°; after drying at 140° it contains $2C^{14}H^8N^2O^4K^2.H^2O$. The *calcium salt*, dried at 140°, appears to have a similar composition. The *silver salt* $C^{14}H^8N^2O^4Ag^2$ is a yellowish-white precipitate, insoluble in water, but easily soluble in ammonia.

Ethyl azobenzoate, $C^{14}H^8N^2O^4(C^2H^5)^2$, obtained by reducing ethylnitrobenzoate with sodium-amalgam in alcoholic solution containing a little free acetic acid, precipitating with water, washing the precipitate with aqueous ammonia, and crystallising it from boiling alcohol, forms long golden-yellow needles melting below 100°, solidifying again in the crystalline form, not volatile without decomposition. It is insoluble in water, but dissolves easily in alcohol and ether. With alcoholic potash it yields potassium azobenzoate; with alcoholic ammonia it forms yellowish laminæ of the amide—probably azobenzamide—which is produced by treating nitrobenzamide with sodium-amalgam. The acid and its salts when ignited with soda-lime give off only half their hydrogen in the form of ammonia.

Para-azobenzoic or *Azodracylic acid*, $C^{14}H^{10}N^2O^4$, is obtained by reducing sodium nitrodracylate with sodium-amalgam, and separates on addition of hydrochloric acid to the yellow solution, as a bulky flesh-coloured precipitate. It melts at above 130°, is sparingly soluble in water, alcohol, and ether, easily in ammonia and fixed caustic alkalis, also in strong sulphuric acid, from which latter solution it is reprecipitated by water. Its *ammonium salt* $2C^{14}H^8N^2O^4(NH^4)^2.H^2O$ forms orange-yellow crystals less soluble in water than the azobenzoate; the *sodium salt* $C^{14}H^8N^2O^4Na^2$ crystallises with difficulty in needles or warty masses; the *barium salt* $C^{14}H^8N^2O^4Ba$, and the *calcium salt* $C^{14}H^8N^2O^4Ca.3H^2O$, are flesh-coloured precipitates; the *silver salt* $C^{14}H^8N^2O^4Ag^2$ is flesh-coloured and amorphous (Reichenbach a. Beilstein, *Ann. Ch. Pharm.* cxxxii. 137; Bilfinger, *ibid.* cxxxv. 152).

The same modification of azobenzoic acid appears to be obtained by reducing an ammoniacal solution of paranitrobenzoic acid with zinc (Sokoloff, *Jahresb.* 1864, p. 344); also, together with oxybenzoic acid, by the action of alcoholic potash on nitrobenzile (Zinin, *ibid.* p. 356):

$$\underset{\text{Nitrobenzile.}}{2C^{14}H^9NO^4} + 4KHO = \underset{\text{Azobenzoate.}}{C^{14}H^8K^2N^2O^4} + \underset{\text{Oxybenzoate.}}{2C^7H^5KO^3} + 2H^2O.$$

The descriptions of the acid thus obtained, and of its salts, do not quite agree with those of the azodracylates above given; but the differences are unimportant, relating chiefly to shades of colour.

HYDRAZOBENZOIC ACID, $C^{14}H^{12}N^2O^4$, is produced by treating a boiling solution of azobenzoic acid in excess of soda-ley with ferrous sulphate, whereupon ferric hydrate is first precipitated, then black ferroso-ferric oxide, and the filtrate yields, on addition of acids, a yellowish-white precipitate of hydrazobenzoic acid. It is likewise easily produced by treating azobenzoic acid in ammoniacal (not in acid) solution with zinc, and (together with azo- and amido- benzoic acids) by treating nitrobenzoic acid with excess of sodium-amalgam. It is insoluble in water, sparingly soluble in hot alcohol, and is precipitated by water from the latter in yellowish-white flocks. With ammonia, potash, or soda it forms yellowish solutions, which absorb oxygen from the air, and are converted into azobenzoates. The warm concentrated ammoniacal solution gives with barium chloride orange-red crystals of the barium salt $C^{14}H^{10}BaN^2O^4$, and with silver nitrate a yellowish precipitate which blackens quickly, with formation of azobenzoic acid. Hydrazobenzoic acid boiled with strong hydrochloric acid is resolved into azobenzoic and amidobenzoic acids: $2C^{14}H^{12}N^2O^4 = C^{14}H^{10}N^2O^4 + 2C^7H^7NO^2$ (Strecker, *loc. cit.*).

Hydrazodracylic acid, $C^{14}H^{12}N^2O^4$, is obtained in like manner by reduction of azodracylic acid, and precipitated by hydrochloric acid as a light flesh-coloured powder, nearly insoluble in water, soluble in hot alcohol, from which it separates on cooling in shining colourless crystals. Its reactions are similar to those of hydrazobenzoic acid. In alkaline solution it is easily oxidised to azodracylic acid. It quickly reduces silver nitrate in presence of ammonia, and is decomposed by boiling hydrochloric acid, with separation of azodracylic acid (Reichenbach a. Beilstein, *Ann. Ch. Pharm.* cxxxii. 137; Bilfinger, *ibid.* cxxxv. 152).

AZO-AMIDOBENZOIC or DIAZOBENZO-AMIDOBENZOIC ACID, $C^{14}H^{11}N^3O^4 = C^7H^4N^2O^2.C^7H^7NO^2$, originally obtained by the action of nitrous acid on amidobenzoic acid (iv. 292), may also be produced by mixing the aqueous solutions of diazobenzoic nitrate and amidobenzoic acid:

$$C^{14}H^{11}N^3O^4.NHO^3 + C^7H^7NO^2 = C^{14}H^{11}N^3O^4 + C^7H^7NO^2.NHO^3.$$

By mixing the aqueous solutions of diazobenzoic nitrate and amidodracylic acid, or of diazodracylic nitrate and amidobenzoic (or amidodracylic) acid, a number of double acids are produced, represented by the formula $C^7H^4N^2O^2.C^7H^7NO^2$, isomeric with the proceding, and very similar to it in their properties (Griess, *Jahresb.* 1864, p. 353).

Azoamidodracylic acid is likewise produced by treating a cold saturated solution of amidodracylic acid with nitrous ether (alcohol saturated with nitrous acid), as a yellow crystalline precipitate, which differs from azoamidobenzoic acid, by yielding, when warmed with strong hydrochloric acid, a red crystalline precipitate of chlorodracylic acid (p. 311) and a solution of amidodracylic hydrochloride:

$$\underset{\text{Azo-amidodracylic.}}{C^{14}H^{11}N^3O^4} + HCl = \underset{\text{Chlorodracylic.}}{C^7H^5ClO^2} + \underset{\text{Amidodracylic.}}{C^7H^7NO^2} + N^2.$$

Nitrous acid passed into a hot alcoholic solution of amidodracylic acid forms benzoic acid and acetic aldehyde, with evolution of nitrogen:

$$\underset{\text{Azo-amidodracylic acid.}}{C^{14}H^{11}N^3O^4} + \underset{\text{Alcohol.}}{2C^2H^6O} + NHO^2 = \underset{\text{Benzoic acid.}}{2C^7H^6O^2} + \underset{\text{Aldehyde.}}{2C^2H^4O} + 2H^2O + 2N^2$$

(Wilbrand a. Beilstein, *Ann. Ch. Pharm.* cxxviii. 257; *Jahresb.* 1863, p. 343).

Azoxybenzoic acid, $C^{14}H^{10}N^2O^5$, is produced, together with aldehyde, by heating an alcoholic solution of nitrobenzoic acid with solid potassium hydrate:

$$2C^7H^5(NO^2)O^2 + 3C^2H^6O = C^{14}H^{10}N^2O^5 + 3C^2H^4O + 3H^2O.$$

The potassium salt separates from the resulting solution as a reddish crystalline mass, and the acid separated therefrom by hydrochloric acid forms (after treatment with animal charcoal) colourless microscopic needles or laminæ, insoluble in water, slightly soluble in alcohol and ether. The acid is bibasic, its salts having the general formula $C^{14}H^8M^2N^2O^5$ or $C^{14}H^8M''N^2O^5$. The barium and silver salts are white crystalline precipitates (Griess, *Ann. Ch. Pharm.* cxxxi. 92).

Respecting the general relations between the azo-derivatives of benzoic acid, see AROMATIC SERIES, p. 210.

Diazobenzoic Acid. $C^7H^4N^2O^2$ (iv. 294).—An aqueous solution of diazobenzoic nitrate or nitrato-diazobenzoic acid mixed with a solution of bromine in hydrobromic acid, deposits an oily precipitate quickly solidifying to yellow prisms of diazobenzoic perbromide, $C^7H^4N^2O^2.HBr.Br^2$. This compound is decomposed by boiling alcohol, in the manner shown by the equation:

$$C^7H^4N^2O^2.HBr.Br^2 = C^7H^5BrO^2 + N^2 + Br^2,$$

yielding bromobenzoic acid identical with that which is produced by the action of bromine on benzoic acid, or of hydrobromic acid on diazo-amidobenzoic acid. The same decomposition takes place, but with strong detonation, when the perbromide is simply heated (Griess, *Ann. Ch. Pharm.* cxxxv. 121; see also Cunze a. Hubner, *ibid.* 106).

Isomeric perbromides with similar properties are produced when the above-mentioned solution of bromine is made to act on the nitric acid compounds of diazodracylic and diazosalylic acids. When boiled with alcohol they also yield the corresponding modifications of monobromobenzoic acid (Griess).

Sulpho-derivatives of Benzoic Acid.

Sulphobenzoic acid, or *Salicyl-sulphurous acid*, $C^7H^6SO^5 = \left.\begin{matrix}(SO)''\\(C^7H^4O)''\\H^2\end{matrix}\right\}O^3$, is described at p. 487, vol. v. Kämmerer a. Carius (*Ann. Ch. Pharm.* cxxxi. 153) have obtained a modification of this acid, which they designate as benzosulphuric acid and represent by the formula $\left.\begin{matrix}(SO^2)''\\(C^7H^4)''\\H^2\end{matrix}\right\}O^3$, as follows: A mixture of silver sulphate with twice its bulk of pounded glass is heated with benzoyl chloride to 140°–150° for a few hours, till the resulting liquid solidifies on cooling to an amorphous transparent mass of benzosulphuric anhydride, $C^{14}H^{10}SO^6$:

$$\left.\begin{matrix}(SO^2)''\\Ag^2\end{matrix}\right\}O^2 + 2(C^7H^5O.Cl) = \left.\begin{matrix}(SO^2)''\\(C^7H^4)''\\C^7H^5O.H\end{matrix}\right\}O^3 + 2AgCl.$$

This anhydride is resolved by solution in warm water into benzoic and benzo-sulphuric acids, the former of which crystallises out:

$$\left.\begin{matrix}(SO^2)''\\(C^7H^4)''\\C^7H^5O.H\end{matrix}\right\}O^3 + H^2O = \left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}O + \left.\begin{matrix}(SO^2)''\\(C^7H^4)''\\H^2\end{matrix}\right\}O^3;$$

and on saturating the warm filtered solution with lead carbonate, decomposing the lead salt with hydrogen sulphide, and evaporating the filtrate at a temperature below 80°, benzosulphuric acid is obtained, as a white crystalline mass melting at 80°, solidifying again in the crystalline form, easily soluble in water and in alcohol, and resolved by boiling its aqueous solution into benzoic and sulphuric acids. From the isomeric compound, sulphobenzoic acid, it is distinguished by the fact that both the free acid and its salts, when treated with phosphorus pentachloride, yield benzo-sulphuric chloride, $C^7H^4Cl^2SO^3 = \left.\begin{matrix}(SO^2)''\\(C^7H^4)''\end{matrix}\right\}\begin{matrix}O\\Cl^2\end{matrix}$, differing in its reactions from the isomeric chloride obtained from sulphobenzoic acid (*infra*).

The metallic benzosulphates are soluble in water, mostly crystallisable, and not decomposed by heating to 150°, or by the boiling of their aqueous solutions. The *ammonium salt* $C^7H^4SO^5(NH^4)^2$ crystallises in radiate groups of needles; the *acid potassium salt* $C^7H^4SO^5.KH$, in fibrous masses permanent in the air (the corresponding sulphobenzoate is efflorescent); the neutral *sodium salt* $C^7H^4SO^5Na^2$ crystallises in tufts of needles; the neutral *barium salt* $C^7H^4SO^5Ba.3H^2O$, in microscopic needles, which slowly give off 1 mol. water over sulphuric acid; the acid *barium salt* $C^7H^4SO^5Ba.C^7H^6SO^5$ is more soluble than the corresponding sulphobenzoate, and forms apparently rhombic, often six-sided prisms. The *lead salt* $C^7H^4SO^5Pb.2H^2O$ crystallises in spherical groups of needles which give off one-fourth of their water at 100°.

Benzosulphuric anhydride, $C^{14}H^{10}SO^6$, is soluble in anhydrous ether, and remains, after evaporation of the solvent, as a light-brown amorphous mass melting at a gentle heat. By solution in water it is decomposed into benzoic and benzosulphuric acids. By excess of benzoyl chloride, it is resolved into benzosulphuric chloride and benzoic anhydride:

$$\left.\begin{matrix}SO^2\\C^7H^4\\C^7H^5O.H\end{matrix}\right\}O^3 + 3C^7H^5OCl = \left.\begin{matrix}SO^2\\C^7H^4\end{matrix}\right\}\begin{matrix}O\\Cl^2\end{matrix} + 2(C^7H^5O)^2O + HCl.$$

With a still larger excess of benzoyl chloride, it yields sulphuryl chloride, SO^2Cl^2, together with other products.

Benzosulphuric chloride, $C^7H^4SO^3Cl^2$, obtained as above or by the action of phosphorus pentachloride on benzosulphuric acid, or by heating silver sulphate with excess of benzoyl chloride to 150°, is a viscid liquid having a pungent odour, especially when warmed. It distils without decomposition at about 300° (sulphobenzoic chloride decomposes at that temperature, v. 488), and is resolved by water into hydrochloric and benzosulphuric acids. Heated with 1 mol. phosphorus pentachloride, it is resolved into sulphuryl chloride and chlorobenzoyl chloride, together with phosphorus trichloride:

$$C^7H^4SO^3Cl^2 + PCl^5 = SO^2Cl^2 + C^7H^4ClO.Cl + PCl^3.$$

With excess of the pentachloride, it yields, instead of chlorobenzoyl chloride, the chloride $C^7H^4Cl^4$, isomeric with chlorosalyl trichloride; at about 180° the sulphuryl chloride is partly decomposed, yielding chloride of sulphur. The isomeric chloride obtained from sulphobenzoic acid, heated with 1 mol. phosphorus pentachloride to 140°–150°, yields sulphurous chloride, chlorobenzoyl chloride, and phosphorus oxychloride:

$$\left.\begin{matrix}SO\\C^7H^4O\end{matrix}\right\}\begin{matrix}O\\Cl^2\end{matrix} + PCl^5 = SOCl^2 + C^7H^4ClO.Cl + POCl^3.$$

Thiobenzoic Acid. $C^7H^6OS = \left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}S = C^6H^5.COSH$ (Engelhardt, Latschinoff a. Malyscheff, *Zeitschr. f. Chem.* [2] iv. 353).—Produced: 1. By the action of benzoyl chloride on potassium monosulphide: $C^7H^5OCl + K^2S = KCl + C^7H^5KOS$.

2. By boiling ethyl or amyl thiobenzoate, thiobenzoic anhydride (benzoyl sulphide), phenyl benzoate, or benzoic anhydride, with an alkaline solution of potassium sulphydrate:

$$\underset{\substack{\text{Ethyl}\\\text{thiobenzoate.}}}{C^7H^5OS.C^2H^5} + KHS = \underset{\text{Mercaptan.}}{C^2H^6S} + \underset{\text{Thiobenzoate.}}{C^7H^5OSK}$$

$$\underset{\substack{\text{Benzoyl}\\\text{sulphide.}}}{(C^7H^5O)^2S} + 2KHS = H^2S + \underset{\text{Thiobenzoate.}}{2C^7H^5OSK}$$

$$\underset{\substack{\text{Phenyl}\\\text{benzoate.}}}{C^7H^5O^2.C^6H^5} + KHS = \underset{\text{Phenol.}}{C^6H^6O} + \underset{\text{Thiobenzoate.}}{C^7H^5OSK}$$

$$\underset{\substack{\text{Benzoic}\\\text{anhydride.}}}{(C^7H^5O)^2O} + 2KHS = H^2S + \underset{\text{Benzoate.}}{C^7H^5O^2K} + \underset{\text{Thiobenzoate.}}{C^7H^5OSK}$$

3. By heating benzoyl sulphide with alcoholic potash or with aqueous ammonia:

$$\underset{\substack{\text{Benzoyl}\\\text{sulphide.}}}{(C^7H^5O)^2S} + 2KHO = H^2O + \underset{\text{Benzoate.}}{C^7H^5O^2K} + \underset{\text{Thiobenzoate.}}{C^7H^5OSK}$$

$$\underset{\substack{\text{Benzoyl}\\\text{sulphide.}}}{(C^7H^5O)^2S} + 2NH^3 = \underset{\text{Benzamide.}}{(C^7H^5O)H^2N} + \underset{\substack{\text{Ammonium}\\\text{thiobenzoate.}}}{C^7H^5OS(NH^4)}$$

4. By heating benzoyl bisulphide with an alcoholic solution of potassium hydrate or sulphydrate.

Thiobenzoic acid is precipitated from the aqueous solution of its potassium salt by hydrochloric acid, as a yellow oil which, when cooled by snow, solidifies to a white radio-crystalline mass, and may be purified by washing with water and drying in the air. It melts at the heat of the hand (about 24°), and has a peculiar sulphurous odour. When exposed to the air it volatilises slightly, apparently with partial decomposition. It may be distilled with vapour of water, but is decomposed by dry distillation, giving off benzoic acid and other products, and leaving a carbonaceous residue. It dissolves easily in alcohol, and in all proportions in ether and in carbon bisulphide, and does not crystallise from solution in a small quantity of either of the two latter liquids, even when cooled by a freezing mixture; but the solution when left to evaporate in contact with the air, deposits a yellowish oil, which gradually solidifies to crystals of benzoyl bisulphide.

A crystalline modification of thiobenzoic acid was obtained by Fleischer (*Ann. Ch. Pharm.* cxl. 234) by prolonged boiling of thiobenzoic aldehyde, C^7H^6S (p. 329), with nitric acid of sp. gr. 1·3. To separate it from the benzoic acid formed at the same time, the liquid was saturated with sodium carbonate, then mixed with hydrochloric acid as long as a yellowish precipitate was produced, and this precipitate after being heated to 160° in a stream of carbonic acid gas was recrystallised from hot water. The thiobenzoic acid thus obtained is more soluble in water than benzoic acid, and separates therefrom as a yellowish crystalline powder; from alcohol or benzol, in tufts of white needles. The crystallised acid $2C^7H^6OS.H^2O$ gives off its water (6·1 p. c.) at 110°, and then becomes less soluble in water. When strongly heated it blackens without melting (Fleischer).

The thiobenzoic acid described by Cloez (v. 775) as a crystalline solid melting at 120° was, according to Engelhardt, Latschinoff a. Malyscheff, nothing but benzoyl bisulphide, $(C^7H^5O)^2S^2$, into which thiobenzoic acid is easily converted by atmospheric oxidation while in the liquid state.

Thiobenzoic acid heated with nitric acid is oxidised to benzoyl bisulphide and benzoic acid. It dissolves in baryta-water and in aqueous sodium carbonate, expelling carbonic acid in the latter case. It dissolves in aqueous ammonia, and on evaporating the solution on the water-bath, the ammonium salt is partially decomposed, with formation of ammonium sulphide.

Potassium thiobenzoate, C^7H^5OSK, prepared as above is very soluble in water, dissolves also in hot alcohol, and crystallises on cooling in large transparent tables and prisms, having a faint yellowish colour. Its aqueous solution mixed with a solution of *iodine* in potassium iodide deposits benzoyl bisulphide:

$$2C^7H^5KOS + I^2 = 2KI + (C^7H^5O)^2S^2.$$

The aqueous solution forms with *cupric sulphate* a greenish-yellow precipitate, which in contact with excess of the reagent gradually acquires a bright red colour; from this red precipitate, carbon bisulphide extracts benzoyl bisulphide. An aqueous solution of the potassium salt forms with *ferric chloride* a violet-brown precipitate, turning yellow when warmed. An alcoholic solution of the potassium salt mixed with ferric chloride acquires a transient violet-brown colour, and soon deposits a white precipitate of benzoyl bisulphide, the ferric chloride being at the same time reduced to ferrous chloride.

The *sodium salt* C^7H^5OSNa, obtained by dissolving the acid in sodium carbonate, is very soluble in alcohol, and separates therefrom on evaporation as an indistinctly crystalline mass. The *barium salt* $(C^7H^5OS)^2Ba$ (at 120°) is also very soluble in alcohol, and separates on evaporation in hydrated laminæ which easily give off their water of crystallisation. The barium salt of Fleischer's thiobenzoic acid is easily soluble in water, sparingly in alcohol, and forms hard crusts made of small nodules containing $(C^7H^5OS)^2Ba . 2H^2O$, which easily give off their water over sulphuric acid. The *lead salt* $(C^7H^5OS)^2Pb$ is a white precipitate insoluble in water, but slightly soluble in boiling carbon bisulphide, and separates on cooling in small slender needles. When warmed it turns black, from formation of lead sulphide. The *silver salt* C^7H^5OSAg is a yellowish-white precipitate insoluble in water. It is but very little decomposed by boiling with water, but if an aqueous solution of the potassium salt be boiled with excess of silver nitrate, and the solution boiled together with the precipitate, the latter soon turns black, being converted into silver sulphide and benzoic acid.

Ethyl thiobenzoate, $C^7H^5OS . C^2H^5$, first obtained by Tütscheff (*Petersb. Acad. Bull.* v. 295) by the action of benzoyl chloride on lead mercaptide, $(C^2H^5S)^2Pb + 2C^7H^5OCl = PbCl^2 + 2(C^7H^5OS . C^2H^5)$, is likewise produced by boiling silver thiobenzoate with ethyl iodide. It is a transparent colourless oily liquid smelling like ethyl benzoate and mercaptan; boils at 243°, is insoluble in water, soluble in alcohol and ether. Boiled with alcoholic solutions of potassium hydrate and sulphydrate, it yields mercaptan, together with benzoate and thiobenzoate of potassium. When boiled with nitric acid, it yields, according to the strength of the acid, benzoic or nitrobenzoic acid, together with ethylsulphurous acid. *Amyl thiobenzoate*, $C^7H^5OS . C^5H^{11}$, obtained by heating amylic mercaptan with benzoyl chloride, is an oily liquid insoluble in water, easily soluble in alcohol and ether; boiling with partial decomposition at 271°. Its reactions are exactly analogous to those of ethyl thiobenzoate.

BENZOYL SULPHIDE OR THIOBENZOIC ANHYDRIDE, $(C^7H^5O)^2S$, is produced by the action of benzoyl chloride on potassium thiobenzoate: $C^7H^5OSK + C^7H^5OCl = KCl + (C^7H^5O)^2S$. The product washed with water and sodium carbonate leaves an oil soluble in ether; and on evaporating the ethereal solution, benzoyl sulphide separates as an oil which solidifies at low temperatures to a crystalline mass, and may be purified by recrystallisation from ether. It is insoluble in water, easily soluble in ether, and separates therefrom by evaporation at low temperatures in large prismatic crystals having a waxy lustre; boils at 48°, and is decomposed by dry distillation, leaving a residue of charcoal, and yielding various oily and crystalline products not yet examined. It dissolves easily in warm aqueous ammonia, forming benzamide and ammonium thiobenzoate; also in alcoholic solution of potassium sulphydrate, with formation of thiobenzoic acid.

BENZOYL BISULPHIDE, $(C^7H^5O)^2S^2$, is obtained by atmospheric oxidation of thiobenzoic acid dissolved in carbon bisulphide or in ether; by oxidising thiobenzoic acid with nitric acid; and by the oxidising action of iodine, cupric sulphate, or ferric chloride on potassium thiobenzoate in aqueous solution. It is also produced, together with the monosulphide $(C^7H^5O)^2S$, by gently heating lead sulphide with benzoyl chloride diluted with ether. Mosling (*Ann. Ch. Pharm.* cxviii. 304) obtained it by the action of hydrogen sulphide on benzoic anhydride. It is conveniently prepared by pouring a solution of iodine in potassium iodide into an aqueous solution of potassium thiobenzoate, dissolving the dried precipitate in boiling carbon bisulphide, from which it separates, by slow cooling or evaporation in a warm place, in large shining prisms or six-sided tables, and by rapid cooling or evaporation in six-sided or rhombic tables. It dissolves with difficulty in boiling ether or alcohol, melts at 128°, and assumes a violet colour when heated a few degrees above its melting point. It is insoluble in water and in aqueous ammonia, not acted upon by nitric acid; dissolves in alcoholic solution of potassium hydrate, with formation of benzoic and thiobenzoic acids; easily in alcoholic solution of potassium sulphydrate, with evolution of hydrogen sulphide and formation of thiobenzoic acid (Engelhardt, Latschineff, a. Malyscheff).

THIOBENZOYL SULPHYDRATE OR DITHIOBENZOIC ACID. $C^7H^6S^2 = \left.\begin{matrix}C^7H^5S \\ H\end{matrix}\right\}S = C^6H^5.CS^2H$ (Engelhardt a. Latschinoff, *Zeitschr. f. Chem.* [2] iv. 455).—Produced by the action of benzotrichloride (p. 282) on potassium monosulphide:

$$\underset{\text{Benzotrichloride.}}{C^6H^5.CCl^3} + 2K^2S = 3KCl + \underset{\text{Potassium dithiobenzoate.}}{C^6H^5.CS^2K}$$

1 mol. benzotrichloride is added to an alcoholic solution of 2 mol. potassium sulphide diluted with a large quantity of alcohol, to moderate the otherwise violent reaction. Chloride of potassium then separates out; the mixture is finally heated over the water-bath to complete the reaction; the red alcoholic solution is filtered, the potassium chloride washed with alcohol; and the united liquids are mixed with water, which throws down a small quantity of resinous substance. The aqueous solution filtered therefrom contains sulphide, dithiobenzoate, and a small quantity of chloride of potassium. On mixing it with lead acetate, a black precipitate of lead sulphide is first formed; and the liquid filtered from this precipitate yields with lead acetate a red precipitate of nearly pure lead dithionate, which may be completely purified by crystallisation from boiling commercial benzol boiling at 122°–130°. The lead salt treated with aqueous solution of potassium or ammonium sulphide yields a precipitate of lead sulphide, and a red solution of potassium or ammonium dithiobenzoate.

Dithiobenzoic acid is also formed as a lead salt, $(C^7H^5S^2)^2Pb$, by treating lead sulphide with benzoyl chloride at a high temperature, whereas if the temperature be kept low, the products of this reaction are benzoyl monosulphide and bisulphide (p. 325); and Fleischer appears to have obtained it as a potassium salt, together with benzylene sulphide, C^7H^6S, by heating benzylene chloride with an alcoholic solution of potassium sulphydrate (p. 281).

Dithiobenzoic acid, $C^7H^6S^2$, is obtained by treating the ammonium or lead salt with hydrochloric acid. It is unstable, quickly decomposing in contact with the air; insoluble in water, easily soluble in ether and in alcohol. A small quantity of it dissolved in ether colours the liquid a splendid carmine-red. When the oily acid, separated from the aqueous solution of the potassium or ammonium salt, is exposed to the air for some time under water, it is converted into a resin insoluble in dilute ammonia, and apparently consisting of a mixture of the compounds $(C^7H^5)^2S^3$ and $(C^7H^5)^2S^4$.

Ammonium dithiobenzoate in aqueous solution has a fine dark orange-red colour, gives with lead acetate a minium-coloured precipitate, with silver nitrate a brown-red, with mercuric chloride a brownish yellow, with bismuth nitrate a red, and with cupric sulphate a black-brown precipitate. The aqueous solution evaporated in contact with the air, decomposes, with separation of a resin similar to that deposited from the solution of the free acid. The *potassium salt* is easily soluble in water, alcohol, and ether, insoluble in carbon bisulphide; the aqueous solution decomposes on evaporation like that of the ammonium salt. The *lead salt* $(C^7H^5S^2)^2Pb$ is insoluble in water, slightly soluble in boiling ether and alcohol, and crystallises from these solutions in very thin orange-red needles; more soluble in boiling carbon bisulphide, and still more in boiling benzol (B. P. 122°–130°), and separates from either of these solutions in beautiful red needles. Boiled with strong hydrochloric acid, it yields dithiobenzoic acid, which may be extracted by ether. Nitric acid oxidises it, with formation of lead sulphate. The *mercuric salt* $C^7H^5S^2Hg$, obtained by precipitation, is insoluble in water, soluble in boiling alcohol, ether, and benzol; crystallises from alcohol in shining laminæ of a reddish golden-yellow colour, like mosaic gold; from benzol in tufts of laminæ having a golden lustre. The *silver salt* $C^7H^5S^2Ag$ is a brown precipitate insoluble in water and in benzol.

Chlorodithiobenzoic acid, $C^6H^4Cl.CS^2H$, is obtained by treating monochlorobenzotrichloride (p. 283) with alcoholic solution of potassium sulphide, the process being conducted similarly to that for the preparation of dithiobenzoic acid. The *lead salt* $(C^7H^4ClS^2)^2Pb$ is a minium-coloured precipitate, which dissolves in boiling benzol and carbon bisulphide, and crystallises therefrom in beautiful red slender needles. When heated with strong hydrochloric acid, it yields the free acid $C^7H^5ClS^2$ as a violet-red oil. The *mercuric salt* $(C^7H^4ClS^2)^2Hg$, obtained by precipitating an ethereo-alcoholic solution of the acid with mercuric chloride, is somewhat less soluble in boiling alcohol than the dithiobenzoate, and crystallises on cooling in small shining laminæ of a greenish-gold colour.

BENZOIC ALDEHYDE. *Benzaldehyde. Benzoyl Hydride. Bitter Almond Oil.* $C^7H^6O = C^6H^5.COH$.—The following modes of formation of this compound have been observed, in addition to those already given (i. 568):

1. By the action of alcoholic potash on benzylene chloride: $C^7H^6Cl^2 + H^2O = 2HCl + C^7H^6O$ (Cahours, *Compt. rend.* lvi. 222).—2. By treating benzylene chloride at ordinary temperatures with strong sulphuric acid, adding water to the mixture and distilling. The reaction is:

$$\begin{aligned} &(1)\quad C^6H^5.CHCl^2 + 2H^2SO^4 = 2HCl + C^6H^5.CH(SO^4H)^2 \\ &(2)\quad C^6H^5.CH(SO^4H)^2 + H^2O = 2H^2SO^4 + C^6H^5.COH \end{aligned}$$

(Oppenheim, *Zeitschr. f. Chem.* [2] v. 441).

3. By heating benzyl chloride to 100° with an equal weight of nitric acid of 27° Bm. diluted with 10 vol. water:

$$C^7H^7Cl + NHO^3 = HCl + NHO^2 + C^7H^6O.$$

A large quantity of benzoic acid is formed at the same time. Benzoic aldehyde is obtained in greater quantity by heating the benzyl chloride (10 grms.) with lead nitrate (14 grms.) and water (100 grms.) to the boiling point for an hour in an atmosphere of carbon dioxide.

4. From benzoic and phthalic acids, by passing their vapours over heated zinc-dust (Baeyer, *Jahresb.* 1866, p. 263); from benzoic acid also by reduction with stannous chloride (Dusart, *ibid.* 1862, p. 263).

5. In small quantity, together with benzene and an unknown substance, by heating a mixture of 1 pt. sodium phthalate and 4 pts. calcium oxalate with 4 pts. calcium hydrate (Dusart).—6. Together with glycocine, by the action of nascent hydrogen on hippuric acid.

7. By heating the silver-compound of dioxindol, $C^8H^6AgNO^2$, the silver being at the same time reduced (Baeyer a. Knop, *Jahresb.* 1866, p. 639).—8. In the germination of the seeds of *Lepidium sativum* (M. Schulze, *ibid.* 1862, 502).

Preparation from Bitter Almonds.—Michael Pettenkofer (*Ann. Ch. Pharm.* cxxii. 77; *Jahresb.* 1862, p. 261) attributes the variation in the yield of oil from the same material to the fact that too little attention is generally paid to ensure the complete dissolution of the amygdalin contained in the almonds, and to prevent the premature decomposition of the emulsin. To obtain a uniform and maximum product, he recommends the following process: 12 pts. of the coarsely pulverised press-cake of bitter almonds (i. 598) are stirred up with 100 to 120 pts. of boiling water; the pasty mass, after being kept at the same temperature for a quarter to half an hour, and then left to cool, is mixed with 1 pt. of the same pulverised press-cake stirred up with 6 to 7 pts. of water; and the mixture, after 12 hours' maceration, is subjected to a moderately rapid distillation. The distillate contains all the volatile oil and prussic acid that can be formed from the amygdalin present: 48 oz. of press-cake yield 7 drms. (nearly 2 p. c.) of bitter almond oil. For the methods of purifying the bitter almond oil from prussic acid, see vol. i. p. 568.

Reactions.—1. Bitter almond oil made up into a paste with *phosphoric anhydride*, in such a manner as not to allow the mixture to get hot, hardens after a few days, and the portion of the mass which is insoluble in warm water dries up on the water-bath to an inodorous resin, resembling colophony, and having, when purified by precipitation of its alcoholic solution with water containing hydrochloric acid, nearly the same composition as the α resin of gum-benzoïn: it yields by dry distillation a thick brownish oil, together with a large quantity of benzoic acid, and by fusion with potash, benzoic and paraoxybenzoic acids (Hlasiwetz a. Barth, *Ann. Ch. Pharm.* cxxxix. 83; *Jahresb.* 1866, p. 632).

2. Bitter almond oil carefully mixed with *sulphuric anhydride* is converted into an acid $C^7H^6SO^4$, whose barium salt $(C^7H^5SO^4)^2Ba$ crystallises in hydrated nodules which give off their water at 170° (Engelhardt, *Jahresb.* 1864, p. 350).

3. Gaseous *hydriodic acid* converts benzoic aldehyde into the compound $C^{21}H^{18}I^4O$

(Geuther a. Cartmell, i. 572); but by heating with 20 pts. of saturated aqueous hydriodic acid, benzoic aldehyde is mainly converted into toluene:

$$C^7H^6O + 4HI = C^7H^8 + H^2O + 2I^2,$$

together with smaller quantities of benzene and carbon dioxide (Berthelot, *Jahresb.* 1867, p. 346).

4. Benzoic aldehyde diluted with coal-tar naphtha (boiling at about 100°) rapidly dissolves *sodium*, producing a compound which separates in gelatinous flocks, and is decomposed by water into benzyl alcohol, C^7H^8O, benzoic aldehyde, and sodium hydrate (Church, *Phil. Mag.* [4] xxv. 522; *Jahresb.* 1863, p. 337). Friedel (*Bull. Soc. Chim.* 1862, p. 18), by treating benzoic aldehyde with sodium-amalgam and water for four or five days, obtained a quantity of benzyl alcohol equal to half the benzoic aldehyde employed. By treating benzoic aldehyde with sodium-amalgam and water in an atmosphere of hydrogen, Church obtained, besides benzyl alcohol, a body which he represents by the formula $C^{14}H^{16}O^2$, and designates as *dicresol*. Claus (*Ann. Ch. Pharm.* cxxxvii. 92), by treating an ethereal solution of benzoic aldehyde with pasty sodium-amalgam for 12 hours, obtained a body having the composition $C^{14}H^{14}O^2$, isomeric with hydrobenzoïn; and Zinin (*ibid.* cxxiii. 125) has obtained hydrobenzoïn by treating benzoic aldehyde with an alcoholic solution of hydrochloric acid and granulated zinc. Claus, in a subsequent paper (*Zeitschr. f. Chem.* [2] iv. 127), regards the body $C^{14}H^{14}O^2$, obtained by the use of sodium-amalgam (with which Church's so-called dicresol is in all probability identical), as *oxybenzylic ether*, $C^6H^5—CHOH—O—CH^2—C^6H^5$, a compound intermediate in constitution between benzyl alcohol and benzoic aldehyde—inasmuch as it may be converted into benzyl alcohol by further treatment with sodium-amalgam, and is easily oxidised to benzoic aldehyde by treatment with chromic acid, even in the cold. This body is also related to benzoic aldehyde, C^7H^6O, in the same manner as pinacone, $C^6H^{14}O$, to acetone, C^3H^6O. When benzoic aldehyde is *heated* with sodium-amalgam, and a stream of carbonic acid gas is passed into the liquid, sodium benzoate is formed, together with an oily liquid, $C^{14}H^{16}O^2$, boiling at 314° (Alexeyeff, *Ann. Ch. Pharm.* cxxix. 347). According to Greville Williams (*Chem. News*, xv. 244), benzoic aldehyde repeatedly treated with *sodium* at a high temperature is converted into toluylene (stilbene), $C^{14}H^{12}$, together with other products:

$$2C^7H^6O + Na^4 = C^{14}H^{12} + 2Na^2O.$$

5. Benzoic aldehyde heated to 100° with *succinyl chloride*, is converted into benzylene chloride and succinic anhydride (Rembold, *Ann. Ch. Pharm.* cxxxviii. 189):

$$C^7H^6O + C^4H^4O^2Cl^2 = C^7H^6Cl^2 + C^4H^4O^3.$$

6. When benzoic aldehyde is left in contact with *ammonium carbamate* in a flask (under an exsiccator), the whole solidifies after some time; and on heating the mass with ether, water, and again with ether, then leaving it for some days between filtering paper, and drying, a colourless, apparently amorphous body is obtained, having the composition of ammonium carbamate with 4 at. H replaced by 2 mol. C^7H^6; thus:

$$\left.\begin{array}{r}H^2\\(CO)''\\NH^4\end{array}\right\}\begin{array}{l}N\\O\end{array} + 2C^7H^6O = 2H^2O + \left.\begin{array}{r}H^2\\(CO)''\\N(C^7H^6)^2\end{array}\right\}\begin{array}{l}N\\O.\end{array}$$

On heating this body with alcohol and filtering, crystals of hydrobenzamide are obtained (E. Mulder, *Zeitschr. f. Chem.* [2] v. 58).

7. A precisely similar action takes place with ammonium oxysulphocarbamate, $\left.\begin{array}{r}H^2\\(CS)''\\NH^4\end{array}\right\}\begin{array}{l}N\\O\end{array}$ (produced by passing carbon-oxysulphide, COS, through alcohol saturated with ammonia), resulting in the formation of the body $\left.\begin{array}{r}H^2\\(CS)''\\N(C^7H^6)^2\end{array}\right\}\begin{array}{l}N\\O\end{array}$, which is also colourless and apparently amorphous, but when heated with alcohol yields a crystallised body different from hydrobenzamide (Mulder, *loc. cit.*).

8. A warm aqueous solution of *amylamine bisulphite*, saturated with benzoic aldehyde, deposits on slow cooling, crystals of hydrated amylamine benzoyl bisulphite, $C^5H^{13}N.SH^2O^3.C^7H^6 + H^2O$, which give off their water in a vacuum over sulphuric acid (H. Schiff, *Zeitschr. f. Chem.* [2] iv. 12).

9. Benzoic aldehyde heated with *acetic anhydride* to 150° for several hours, unites with it, forming the compound $C^{11}H^{12}O^4 = C^7H^6(C^2H^3O^2)^2$, identical with benzylene biacetate (i. 578). When purified by distilling the product, and washing the

portion which passes over above the boiling point of benzoic aldehyde with aqueous sodium bisulphite, it remains as an oil, which quickly solidifies to a crystalline mass, melting at 45°, very easily soluble in alcohol and ether, and distinguished by its great tendency to crystallise (Geuther, *Ann. Ch. Pharm.* cvi. 249; Hübner, *Bull. Soc. Chim.* [2] viii. 459; Perkin, *Chem. Soc. J.* [2] v. 586).

10. With *acetyl chloride*, benzoic aldehyde forms cinnamic (phenyl-acrylic) acid:

$$C^2H^3OCl + C^7H^6O = HCl + C^9H^8O^2$$

(Bertagnini, *Ann. Ch. Pharm.* c. 125). With *butyryl chloride*, in like manner, it forms phenyl-angelic acid (Fittig a. Bieber, *Zeitschr. f. Chem.* [2] v. 333):

$$C^4H^7OCl + C^7H^6O = HCl + C^{11}H^{12}O^2.$$

11. When bitter almond oil containing *prussic acid* is left in contact in a closed flask for two hours with aqueous *hydrochloric acid* saturated at 8°, the watery and oily liquids then shaken together, while the vessel is kept cool by immersion in cold water, the whole again left to itself for 24 hours, and once more shaken up, the liquids solidify together to a mass of crystals consisting of dibenzoyl-hydrocyanide, $(C^7H^6O)^2.CNH$. This compound is nearly insoluble in boiling water, slightly soluble in boiling alcohol. ether. and benzol, and crystallises from alcohol or glacial acetic acid in small prisms melting at 195°, and decomposing when volatilised into an oil and charcoal. Heated with aqueous hydrochloric acid to 120°, it decomposes, with formation of benzoic aldehyde, mandelic acid (?), and sal-ammoniac. Heated with water or alcohol to 180°, it is entirely resolved into benzoic aldehyde and mandelamide, $C^8H^9NO^2$:

$$(C^7H^6O)^2.CNH + H^2O = C^7H^6O + C^6H^5.CH(OH).CONH^2,$$

which crystallises from water in rhombic or hexagonal tables (Zinin, *Zeitschr. f. Chem.* [2] iv. 709).

12. The yellow resinous body produced by prolonged contact of *ammonia* with bitter almond oil containing prussic acid was examined by Laurent and by Gerhardt, who obtained from it various products, according to the circumstances of its formation (i. 599). Th. Müller a. H. Limpricht (*Ann. Ch. Pharm.* cxi. 136) have examined the product obtained by the action of ammonia on that portion of crude bitter almond oil which remains in the retort after distillation at 184°. The yellow resin thus formed is resolved by ether into an insoluble portion containing hydrobenzamide and other bodies. and a solution which, on addition of alcohol, deposits a large quantity of a crystalline substance, not exhibiting a constant composition, even after repeated crystallisation from alcohol. Its alcoholic solution mixed with hydrochloric acid gives off hydrocyanic acid, and yields needle-shaped crystals of a hydrochloride $C^{14}H^{16}N^2.2HCl$, from which potash separates a base, $C^{14}H^{16}N^2$, crystallising from dilute alcohol in shining laminæ melting at 122°. The *sulphate* $C^{14}H^{16}N^2.H^2SO^4$ crystallises in needles; the *platinum salt* $C^{14}H^{16}N^2.2HCl.PtCl^4$ is a yellow precipitate.

Parachlorobenzoic aldehyde, $C^6H^4Cl.COH$, is produced by prolonged boiling of chlorobenzyl chloride, $C^6H^4Cl.CH^2Cl$, with lead nitrate and water; more easily by heating chlorobenzylene chloride, $C^6H^4Cl.CHCl^2$, with water in a sealed tube. When separated from its compound with sodium bisulphite, it is an oil which boils without decomposition, smells like bitter almond oil when cold, and when heated gives off a strongly tear-exciting vapour (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2] iii. 467). The same compound is obtained by distilling chlorotribenzylamine, $(C^7H^6Cl)^3N$, with bromine and water. (See BENZYLAMINES.) It passes over with the aqueous vapour, and when purified as above, boils between 210° and 220°. When exposed to the air it quickly absorbs oxygen, and is converted into parachlorobenzoic acid (Berlin, *Ann. Ch. Pharm.* cli. 140).

Tetrachlorobenzoic aldehyde, $C^6HCl^4.COH$, appears to be produced by heating the chloride $C^6HCl^4.CH^2Cl$ with water to 280° (Beilstein a. Kuhlberg, *Zeitschr.* [2] v. 528).

THIOBENZOIC ALDEHYDE OF THIOBENZOYL HYDRIDE, $C^7H^6S = C^6H^5.CSH$, the compound which Laurent obtained by the action of ammonium sulphide on an alcoholic solution of bitter almond oil (i. 571), is probably identical with the benzylene sulphide or sulphobenzol which Cahours obtained by treating benzylene chloride, $C^7H^6Cl^2$, in alcoholic solution with potassium sulphydrate (i. 577), although Laurent's product is described as a white powder softening at 90°–95°, whereas that obtained by Cahours crystallised in micaceous scales melting at 64°. The latter product has been further examined by Fleischer (*Ann. Ch. Pharm.* cxl. 234), who finds that it melts at 68°–70°, and decomposes at a higher temperature, yielding toluylene or stilbene, $C^{14}H^{12}$, thionessal, $C^{28}H^{18}S$ (the products of decomposition obtained by Laurent), together with tolallyl sulphide, $C^{14}H^{14}S$. It dissolves easily in ether and benzol, less easily in alcohol, and crystallises from the latter in white shining laminæ, from ether in transparent prisms. The alcoholic solution does not unite with mercuric oxide; with *mercuric chloride* and *lead acetate*, it forms precipitates which quickly decompose. *Bromine* produces in the ethereal solution a brown oil, which strongly attacks the mucous membranes. *Nitric acid* of sp. gr. 1·3 converts it into a yellowish oil, and, after prolonged boiling, forms, together with sulphuric and benzoic acids, a peculiar modification of thiobenzoic acid, C^7H^6OS (p. 324).

In preparing the compound C^7H^6S by the action of potassium sulphydrate on benzylene chloride, Fleischer likewise obtained dithiobenzoic acid, $C^7H^6S^2 = C^7H^5S.HS$ (p. 326), perhaps in consequence of the presence of potassium bisulphide in the sulphydrate. It remained in solution after the monosulphide had been thrown down by water, and was separated therefrom by hydrochloric acid as a red non-crystallising oil having a fetid odour.

Parachlorothiobenzoic aldehyde, $C^6H^4Cl.CSH$, separates on passing dry sulphydric acid gas into the alcoholic solution of parachlorobenzoic aldehyde, as a pale rose-coloured flocculent precipitate, insoluble in alcohol, but easily soluble in benzol, and remaining on evaporation of that solvent as a transparent varnish (Beilstein a. Kuhlberg).

BENZOIC CHLORIDE or **BENZOYL CHLORIDE.** $C^7H^5OCl = C^6H^5.COCl$ (i. 566).—This compound is produced synthetically by the action of carbonyl chloride on benzene in sunshine: $C^6H^6 + COCl^2 = HCl + C^7H^5OCl$ (Harnitz-Harnitzky, *Bull. Soc. Chim.* [2] iii. 322). It is formed also by the action of sulphur dichloride, S^2Cl^2, on sodium benzoate, or at a high temperature on benzoic acid (Carius, *Ann. Ch. Pharm.* cvi. 291). Red chloride of sulphur likewise converts sodium benzoate into benzoyl chloride (Heintz). Beketoff (*ibid.* cix. 256) obtained benzoyl chloride in small quantity by heating a mixture of benzoic acid, sodium chloride, and sodium anhydrosulphate to 200°:

$$C^7H^6O^2 + SO^3 + 2NaCl = C^7H^5OCl + HCl + Na^2SO^4.$$

Lastly, benzoyl chloride is formed, together with other products, by the action of phosphorus pentachloride on hippuric acid (Schwanert, iii. 158).

Reactions.—1. Benzoyl chloride is not acted upon by *chlorine*, even at the boiling heat (Grimaux a. Vogt, *Dict. de Chimie*, i. 569)—2. By treating benzoyl chloride with *phosphorus pentachloride*, Limpricht (*Ann. Ch. Pharm.* xcix. 171) has obtained the compounds $C^7H^4Cl^4$ and $C^7H^3Cl^5$, in addition to the trichloride $C^7H^5Cl^3$ previously obtained by Schischkoff a. Rosing (i. 567).

3. Benzoyl chloride treated with *potassium monosulphide* in alcoholic solution, is converted into thiobenzoic acid, and by heating with lead sulphide into benzoyl bisulphide (p. 325).—4. With *sulphuric anhydride* it unites directly, forming sulphobenzoic chlorhydrate, $C^7H^5ClSO^4$ (v. 488) (Engelhardt, *Jahresb.* 1864, p. 949).—5. Heated to 140°–150° with caustic baryta, it yields benzoic anhydride, the reaction doubtless consisting in the first instance in the formation of barium chloride and barium benzoate, from which the benzoic anhydride is formed by the action of the benzoyl chloride (H. Gal, *Jahresb.* 1863, p. 337). A similar reaction, but less complete, takes place with lead oxide.—6. With *barium dioxide*, BaO^2, benzoyl chloride yields benzoyl peroxide, $(C^7H^5O)^2O^2$ (Brodie, iv. 310).

7. Benzoyl chloride is not attacked by *potassium* or *sodium* at ordinary temperatures; but when its solution in anhydrous ether is heated with sodium for 24 hours in the water-bath, the ether deposits small crystals of dibenzoyl, $(C^7H^5O)^2$ (Briegel, *Bull. Soc. Chim.* [2] v. 278).—8. When dry *hydrochloric acid gas* is slowly passed through liquid *sodium amalgam* (containing but little sodium) covered with a layer of benzoyl chloride, benzoic aldehyde is first produced, and this by further addition of hydrogen is converted into benzyl alcohol (Lippmann, *ibid.* iv. 249).

9. *Potassamide* introduced into a solution of benzoyl chloride in anhydrous ether forms benzamide and dibenzamide (Baumert a. Landolt, *Ann. Ch. Pharm.* cxi. 1):

$$\underset{\substack{\text{Benzoyl}\\\text{chloride.}}}{3C^7H^5OCl} + 3KNH^2 = \underset{\text{Benzamide.}}{C^7H^7NO} + \underset{\text{Dibenzamide.}}{C^{14}H^{11}NO^2} + 3KCl + NH^3.$$

10. With *argentammonium sulphate* (an ammoniacal solution of silver-oxide mixed with sulphuric acid) benzoyl chloride forms ammonium sulphate, silver chloride, and benzamide (Engelhardt, *Ann. Ch. Pharm.* cviii. 386):

$$(NH^3Ag)^2SO^4 + 2C^7H^5OCl = 2(NH^2.C^7H^5O) + H^2SO^4 + 2AgCl.$$

11. Benzoyl chloride heated with *potassium cyanate* gives off a small quantity of

benzonitrile, C^7H^5N, and leaves cyaphenine, $C^{21}H^{15}N^3$ (a solid substance polymeric therewith), mixed with potassium chloride (Cloez, *Bull. Soc. Chim.* 1859, p. 100).—12. With *zinc ethyl* it forms benzoyl-ethyl, $C^7H^5O.C^2H^5$, which separates on addition of water as a fragrant liquid boiling at 117° (Freund, *Ann. Ch. Pharm.* cxviiii. 1).—13. With the zinc-salt of *amidobenzoic acid* it forms benzo-amidobenzoic acid, $C^7H^4(C^7H^5O)NO^2$ (Foster, iv. 292).—14. Heated to 200° in a sealed tube with *ethyl succinate*, it yields succinic anhydride, ethyl benzoate, and ethyl chloride (Kraut, *Ann. Ch. Pharm.* cxxxvii. 254):

$$\left.\begin{matrix}C^4H^4O^2\\(C^2H^5)^2\end{matrix}\right\}O^2 + C^7H^5OCl = C^4H^4O^2.O + \left.\begin{matrix}C^7H^5O\\C^2H^5\end{matrix}\right\}O + C^2H^5Cl.$$

15. *Isethionates* are converted by benzoyl chloride into benzoyl-isethionates, e.g.,

$$C^2H^4(KSO^3)OH + C^7H^5OCl = HCl + C^2H^4(KSO^3)OC^7H^5O.$$

With *ethyl sulphates* a totally different reaction takes place, resulting in the formation of ethyl chloride. With *sulphanilic acid*, in like manner, it forms benzoylsulphanilic acid, $C^6H^4(HSO^3)(C^7H^5O)N$ (Engelhardt a. Latschinoff, *Zeitschr. f. Chem.* [2] iv. 234, 266.)

16. Benzoyl chloride unites directly with *nicotine*, forming the compound $C^{10}H^{14}N^2.2C^7H^5OCl$, which may be regarded as hydrochloride of benzoyl-nicotine, $\left.\begin{matrix}(C^{10}H^{12})^{iv}\\(C^7H^5O)^2\end{matrix}\right\}N^2.2HCl$, or chloride of benzoyl-nicotammonium, $\left.\begin{matrix}(C^{10}H^{14})^{iv}\\(C^7H^5O)^2\end{matrix}\right\}N^2.Cl^2$ (H. Will, *Ann. Ch. Pharm.* cxviii. 206).—17. With *hydroxylamine*, $NH^2(OH)$, it forms dibenzhydroxamide, $N(C^7H^5O)^2OH$ (C. A. Heintz, *Zeitschr. f. Chem.* [2] v. 733).

Chlorobenzoyl chloride, $C^7H^4ClO.Cl$, is produced by the action of 1 mol. phosphorus pentachloride on benzosulphuric chloride, $C^7H^4SO^3Cl^2$ (Kämmerer a. Carius, p. 323); and by gently heating 1 mol. quinic acid, $C^7H^{12}O^6$, with 5 mol. phosphorus pentachloride (Graebe, *Ann. Ch. Pharm.* cxxxviii. 197):

$$C^7H^{12}O^6 + 5PCl^5 = C^7H^4ClO.Cl + 5POCl^3 + 8HCl.$$

Metachlorobenzoyl chloride, or *Chlorosalyl chloride*, $C^7H^4ClO.Cl$, isomeric with the preceding, is the compound which Chiozza obtained by the action of phosphorus pentachloride on salicylic acid (i. 568: there called *chloride of parachlorobenzoyl*). It is transformed by water into metachlorobenzoic or chlorosalylic acid; by ammonia into chlorosalylamide; by aniline into chlorosalylanilide. According to Kekulé (*Ann. Ch. Pharm.* cxvii. 145), it is partly decomposed at each distillation, becoming richer in chlorine the oftener it is rectified.

BENZOIC OXIDE or **ANHYDRIDE**. $(C^7H^5O)^2O$.—This compound is produced, according to Gal (p. 330), by heating benzoyl chloride with barium oxide to 140°–150° for twenty hours. Its specific gravity in the liquid state is 1·227 at 27° and 1·206 at 25·8° (Mendelejef, *Jahresb.* 1858, p. 274). Heated in dry hydrochloric acid gas, it is resolved into benzoic acid and benzoyl chloride:

$$(C^7H^5O)^2O + HCl = C^7H^5O.HO + C^7H^5OCl.$$

By prolonged heating in dry sulphydric acid gas it yields a distillate of benzoic acid, mixed with oily drops apparently consisting of benzoic aldehyde and a residue of benzoyl bisulphide (Mosling, *Ann. Ch. Pharm.* cxviii. 303):

$$3(C^7H^5O)^2O + 2H^2S = 3(C^7H^5O.HO) + C^7H^5O.H + (C^7H^5O)^2S^2.$$

Benzo-iodic oxide or **Iodine benzoate**, $C^7H^5IO^2 = \left.\begin{matrix}C^7H^5O\\I\end{matrix}\right\}O$, has not been obtained pure, but appears to be formed, together with sodium chloride, by the action of iodine chloride on sodium benzoate: $C^7H^5NaO^2 + ICl = NaCl + C^7H^5IO^2$. On heating the product of this reaction, carbon dioxide and iodine are given off, and a liquid distils over which is resolved by fractional distillation into iodobenzene, C^6H^5I, and a solid body resembling naphthalene (Schützenberger, *Compt. rend.* lii. 135; *Jahresb.* 1861, p. 349).

Benzoic Peroxide, $(C^7H^5O)^2O^2$, is described in vol iv. p. 310.

BENZOIC SULPHYDRATE, $C^7H^5O.SH$, **SULPHIDE**, $(C^7H^5O)^2S$, and **BISULPHIDE**, $(C^7H^5O)^2S^2$, have already been described among the SULPHUR-DERIVATIVES OF BENZOIC ACID (pp. 324–326).

BENZOÏN. $C^{14}H^{12}O^2$.—This body, polymeric with benzoic aldehyde, is easily prepared from benzile, $C^{14}H^{10}O^2$, by the action of reducing agents, as when a solution of 1 pt. benzile in 6 pts. acetic acid of sp. gr. 1·065 is boiled with 1 or 2 pts. of metallic iron. The liquid then coagulates to a pulp of needle-shaped crystals of benzoïn; and by decanting these crystals from the residual iron, washing them, after cooling, with water, and crystallising from alcohol, benzoïn is obtained perfectly pure. A warm alcoholic solution of benzile is also converted into benzoïn by treatment with finely granulated zinc and hydrochloric acid. By further continuance of the reducing action in this latter case, the benzoïn is converted into a body richer in hydrogen (iii. 185) (Zinin, *Ann. Ch. Pharm.* cxix. 177; cxxiii. 125).

Benzoïn boiled with alcoholic *potash* is almost wholly converted into potassium benzilate: $C^{14}H^{12}O^{2} + KHO = C^{14}H^{11}KO^{2} + H^{2}$ (the hydrogen being oxidised in contact with the air); but when heated with alcoholic potash to 150°–160° in a sealed and exhausted tube, it yields benzilic acid, hydrobenzoïn, and the body isomeric (? identical) therewith which Claus obtained by the action of sodium-amalgam on an ethereal solution of benzoic aldehyde (Zinin, *Bull. Soc. Chim.* [2] vii. 260). Heated to 100° with alcoholic *ammonia*, it is resolved into benzoïnam, $C^{14}H^{34}N^{2}O$, lophine, $C^{21}H^{16}N^{2}$, and a resinous body, accompanied by small quantities of benzoïnimide, $C^{14}H^{11}N$, and a granular substance (J. Erdmann, *Ann. Ch. Pharm.* cxxxv. 181). Heated with *aniline* to 200°, it is converted into a crystalline substance apparently identical with the so-called benzoyl-anilide, $C^{13}H^{11}N$, which Laurent a. Gerhardt obtained by the action of aniline on benzoic aldehyde. This body is probably ditoluidene-diphenamine, $C^{26}H^{22}N^{2} = (C^{7}H^{6})^{2}(C^{6}H^{5})^{2}N^{2}$ (Schiff, *Jahresb.* 1865, p. 413).

Benzoïn heated for seven or eight hours to 130° with 1½ pts. of hydrochloric acid saturated at 8°, is converted into an oily body, which floats on the acid, and on opening the tube solidifies to a laminar mass, separable by the action of solvents into lepidene, $C^{28}H^{20}O$, which remains for the most part undissolved on treating the product with ether; benzyl, $C^{14}H^{14}$, which crystallises from the ethereal solution, and a thick oil insoluble in water, easily soluble in alcohol and ether (Zinin, *Bull. Soc. Chim.* [2] viii. 271).

Deoxybenzoïn. $C^{14}H^{12}O$ (Zinin, *Ann. Ch. Pharm.* cxix. 179; cxxvi. 218; *Zeitschr. f. Chem.* [2] iv. 718).—Produced from benzoïn by the action of nascent hydrogen evolved by zinc and hydrochloric acid; more easily by similar treatment of chlorobenzile dissolved in alcohol:

$$C^{14}H^{10}Cl^{2}O + 2HCl + Zn^{2} = 2ZnCl^{2} + C^{14}H^{12}O.$$

Deoxybenzoïn, purified by crystallisation from ether and alcohol, is white, easily soluble in alcohol and in ether, slightly soluble in boiling water, from which it separates as an oil, or in needles and laminæ resembling benzoic acid. It melts in capillary tubes at 45°, but in larger masses at a higher temperature, and then solidifies at 53° to a crystalline broadly laminar mass. It is not altered by potash, either in aqueous or in alcoholic solution, or by benzoyl chloride.

Deoxybenzoïn is strongly attacked by *bromine*, forming the compound $C^{14}H^{10}Br^{2}O$, analogous to chlorobenzile (p. 305), and crystallising in rhombic prisms melting at 87°, decomposing at a higher temperature. This componnd treated with silver nitrate or fuming nitric acid yields benzile; with alcoholic potash, it yields potassium benzoate and benzoic aldehyde.

The action of chlorine on deoxybenzoïn is not so definite as that of bromine. The product, which does not resemble chlorobenzile, is dissolved by alcoholic potash, with formation of benzoic or benzilic acid.

With *phosphorus pentachloride*, deoxybenzoïn forms an oily body, $C^{14}H^{11}Cl$, insoluble in water, soluble in alcohol and ether:

$$C^{14}H^{12}O + PCl^{5} = C^{14}H^{11}Cl + POCl^{3} + HCl:$$

and this substance treated with sodium-amalgam and water yields toluylene or stilbene:

$$C^{14}H^{11}Cl + Na^{2} + H^{2}O = C^{14}H^{12} + NaCl + NaHO.$$

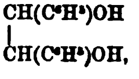
The same substance distilled or merely heated to boiling with caustic potash yields crystals of tolane, $C^{14}H^{10} = C^{14}H^{11}Cl + HCl$.

Descxybenzoïn heated with *nitric acid* of sp. gr. 1·2 is converted into paranitrobenzoic acid (p. 314).

Deoxybenzoïn may be regarded as the anhydride of hydrobenzoïn, $C^{14}H^{14}O^{2} - H^{2}O = C^{14}H^{12}O$; it appears to be identical with hydrobenzile produced by the action of ammonium sulphide on benzile (iii. 185), and with oxide of toluylene or stilbene, which, according to Limpricht a. Schwanert (*Jahresb.* 1867, p. 675), is produced by heating toluylene acetate with alcoholic potash, and crystallises in needles melting at 58°.

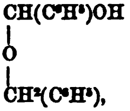
Hydrobenzoïn, $C^{14}H^{14}O^{2}$, originally obtained by treating pure benzoic aldehyde with zinc and hydrochloric acid (iii. 185), and subsequently by heating benzoïn with alcoholic potash in sealed tubes (*supra*), is identical with toluylenic or stilbenic alcohol:

$(C^{14}H^{12})''(HO)^{2}$ or



$$\begin{array}{l} CH(C^{6}H^{5})OH \\ | \\ CH(C^{6}H^{5})OH, \end{array}$$

produced from toluylene bromide, $C^{14}H^{12}Br^2$, by heating that compound with silver acetate or oxalate, whereby it is converted into the corresponding acetate or oxalate, and treating either of these ethers with alcoholic potash (Limpricht a. Schwanert, *Zeitschr. f. Chem.* [2] iii. 684); probably also with the compound of the same composition obtained by the action of sodium-amalgam on benzoic aldehyde (Claus; Church, p. 328), or on benzoic acid (Hermann, *Ann. Ch. Pharm.* cxxxii. 75). It is true that the melting points of these several products do not quite agree, Zinin's hydrobenzoïn melting at 130°, Church's so-called dicresol at 129°, Claus's product at 100°, and Hermann's at 116°, and the toluylenic alcohol of Limpricht a. Schwanert at 122°; but these differences may be due to the various degrees of purity of the several products. Claus, as already observed, regards his product as *oxybenzylic ether*:



$$\begin{array}{l} CH(C^6H^5)OH \\ | \\ O \\ | \\ CH^2(C^6H^5), \end{array}$$

and as different from hydrobenzoïn, because it gives different reactions (not specified) with nitric acid, and because it reacts like a body intermediate between an alcohol and an aldehyde, being converted into benzylic alcohol by nascent hydrogen, and into benzoic aldehyde by oxidation with chromic acid. But hydrobenzoïn exhibits very similar characters, being also converted by nascent hydrogen into benzyl-alcohol, which, indeed, is always formed simultaneously with it, and by oxidation with nitric acid into benzoïn, polymeric with benzoic aldehyde.

BENZOLEIC ACID. $C^7H^{10}O^2$. *Hydrobenzoic Acid* (Hermann, *Ann. Ch. Pharm.* cxxxii. 75; Otto, *ibid.* cxxxiv. 303).—This acid, intermediate between benzoic and œnanthylic acids, is obtained: 1. By the action of nascent hydrogen on benzoic acid. When this acid is boiled with a little water, sodium-amalgam added, and a current of hydrochloric acid gas directed into the mixture, sodium benzoleate is produced, together with benzyl alcohol, and a compound containing $C^{14}H^{14}O^2$ (? hydrobenzoïn). The benzyl alcohol is separated by distillation; the residue is agitated with ether to remove the compound $C^{14}H^{14}O^2$; and the remaining sodium benzoleate is decomposed by hydrochloric acid. Benzoleic acid then separates as an oil which does not solidify in the cold, provided all the benzoic acid has been converted into benzoleic acid; in the contrary case, the treatment with nascent hydrogen must be repeated (Hermann).—2. By heating hydrobenziluric acid, $C^{16}H^{21}NO^4$ (produced by the action of nascent hydrogen on hippuric acid), with a strong solution of caustic alkali:

$$\underset{\text{Hydrobenziluric acid.}}{C^{16}H^{21}NO^4} + H^2O = \underset{\text{Benzoleic acid.}}{C^7H^{10}O^2} + \underset{\text{Glycocine.}}{C^2H^5NO^2} + \underset{\text{Benzyl alcohol.}}{C^7H^8O}$$

Benzoleic acid is a rather mobile, volatile, acid oil, having a disagreeable odour somewhat like that of valerianic acid; heavier than water, insoluble therein, very soluble in alcohol and ether. It does not unite readily with bases; nevertheless when heated with alkaline carbonates it expels the carbonic acid. It is very unstable.

The *benzoleates* of *sodium* and *calcium* are deliquescent, alterable on exposure to the air, slightly soluble in boiling alcohol, separating out as the solution cools. According to Otto, the calcium salt is converted by repeated crystallisation, into benzoate, with loss of 4 at. hydrogen. *Ethyl benzoleate*, $C^7H^9(C^2H^5)O^2$, obtained by passing hydrochloric acid gas into an alcoholic solution of benzoleic acid, is a transparent colourless liquid, smelling like ethyl valerate, and decomposing when exposed to the air (Hermann).

BENZONE or **BENZOPHENONE.** Syn. with PHENYL-BENZOYL (iv. 478).

BENZONITRILE or *Phenyl Cyanide*. See CYANIDES.

BENZOPINACONE. See PINACONE (iv. 648).

BENZOYL. C^7H^5O.—The radicle of the benzoic series. In the free state, as $C^{14}H^{10}O^2$, sometimes called *Dibenzoyl*, it is obtained by treating benzoic chloride dissolved in ether with sodium-amalgam, the action being assisted towards the end by the heat of a water-bath. The solution, filtered after 24 hours, shaken up with water to decompose the remaining portion of benzoic chloride, then freed from the greater part of the ether by distillation, and left to stand in a closed vessel, gradually deposits small crystals of benzoyl, which may be purified by recrystallisation from ether. Benzoyl forms small colourless prisms having a vitreous lustre, melting at 146°, subliming without decomposition, and only slightly soluble in alcohol and in ether. It dissolves in strong sulphuric acid, and separates on addition of water, apparently without alteration, in long slender needles. When boiled with alcoholic potash, it decomposes, with formation of benzoic acid, and an oily body precipitable by water, which is probably benzyl alcohol, this latter body being formed by a secondary reaction from benzoic aldehyde, which is probably formed in the first instance, together with benzoic acid:

$$\underset{\text{Benzoyl.}}{C^{14}H^{10}O^2} + KHO = \underset{\substack{\text{Potassium}\\ \text{benzoate.}}}{C^7H^5KO^2} + \underset{\substack{\text{Benzoic}\\ \text{aldehyde.}}}{C^7H^6O}$$

This behaviour, together with the melting point and solubility, distinguish benzoyl from benzile (melting at about 90°), with which it is isomeric (Brigel, *Ann. Ch. Pharm.* cxxxv. 171).

BENZOYL CHLORIDE. See BENZOIC CHLORIDE.

BENZOYL HYDRIDE. See BENZOIC ALDEHYDE.

BENZYL, C^7H^7; in the free state, $C^{14}H^{14}$ (dibenzyl).—The preparation and properties of this radicle are described in vol. v. p. 870, where the name *benzyl* is used as synonymous with *tolyl*. Fittig, however, has shown (*Ann. Ch. Pharm.* cxxxix. 178) that tolyl, $C^{14}H^{14}$, obtained by heating bromotoluene with sodium, is isomeric, not identical, with benzyl produced in like manner from benzyl chloride, tolyl being a liquid, whereas benzyl is a crystalline solid. The isomerism between benzyl and tolyl is exhibited by the following formulæ:

$$C^6H^4\begin{cases}CH^2Cl\\ H\end{cases}$$

Benzyl chloride.

$$C^6H^4\begin{cases}CH^3\\ Cl\end{cases}$$

Chlorotoluene.

$$C^6H^4\begin{cases}CH^2[CH^2(C^6H^5)]\\ H\end{cases}$$

Dibenzyl.

$$C^6H^4\begin{cases}CH^3\\ C^6H^4(CH^3).\end{cases}$$

Ditolyl.

Benzyl is also produced by heating toluylene, $C^{14}H^{12}$, to 140°–150° with concentrated hydriodic acid, and may be separated by washing the product with soda-ley and water, and recrystallising from alcohol. It melts at 48°–50° (Limpricht a. Schwanert, *Ann. Ch. Pharm.* cxlv. 330).

When passed in the state of vapour through a red-hot tube filled with fragments of pumice, it is resolved into toluene and toluylene: $2C^{14}H^{14} = 2C^7H^8 + C^{14}H^{12}$ (R. Otto, *Zeitschr. f. Chem.* [2] vi. 22).

Benzyl bromide, $C^6H^5.CH^2Br$, *Benzyl chloride*, $C^6H^5.CH^2Cl$, and their substitution derivatives, are described in association with their isomerides, the bromo- and chloro- toluenes (v. 853–856, and pp. 280–284 of this volume).

Brominated substitution products of Dibenzyl were obtained by Stelling and Fittig (v. 871) by the action of bromine on benzyl suspended in water. Limpricht a. Marquart (*Zeitschr. f. Chem.* [2] v. 337) have obtained compounds isomeric with these by treating benzyl with *dry* bromine. *Monobromodibenzyl*, $C^{14}H^{13}Br$, thus obtained, is an oil, which when heated with alcoholic potash yields toluylene: $C^{14}H^{13}Br - HBr = C^{14}H^{12}$. The *dibromodibenzyl*, $C^{14}H^{12}Br^2$, produced in like manner, is identical with toluylene bromide, and like that compound is converted by alcoholic potash into tolane, $C^{14}H^{10}$. The *tribromodibenzyl* could not be separated completely from the preceding compound; but it is essentially different from the tribrominated compound produced by treating dibenzyl with bromine in presence of water.

Benzyl, therefore, exhibits the same tendency as toluene, xylene, &c., to yield, with bromine or chlorine, different products accordingly as the reaction takes place at low or at high temperatures, the substitution of the bromine in dibenzyl as well as in toluene taking place within the phenyl molecule at low temperatures, and in the methyl molecule (the lateral chain) at high temperatures.

BENZYL ALCOHOL. $C^7H^8O = C^6H^5.CH^2OH$.—Isomeric with cresol. Described in vol. i. p. 578. Produced also: 1. Together with hydrobenzoïn and ethyl benzoleate, by the action of sodium-amalgam on benzoic acid (Hermann, p. 328).—2. Together with glycocine, hydrobenzoïn, and a nitrogenous acid, by the action of sodium-amalgam on hippuric acid (Hermann, *Ann. Ch. Pharm.* cxxxiii. 355; *Jahresb.* 1865, p. 354).—3. By boiling hydrobenzyluric acid (produced by adding sodium-amalgam to a concentrated alkaline solution of hippuric acid) with alkalis:

$$\underset{\substack{\text{Hydrobenzyluric}\\ \text{acid}}}{C^{16}H^{21}NO^4} + H^2O = \underset{\text{Glycocine}}{C^2H^5NO^2} + \underset{\substack{\text{Benzyl}\\ \text{alcohol}}}{C^7H^8O} + \underset{\substack{\text{Benzoleic}\\ \text{acid;}}}{C^7H^{10}O^2}$$

and in like manner from hydroxybenzyluric acid:

$$\underset{\text{Hydroxybenzyluric acid.}}{2C^{16}H^{21}NO^{5}} + H^{2}O = \underset{\text{Glycocine.}}{2C^{2}H^{5}NO^{2}} + \underset{\text{Benzyl alcohol.}}{2C^{7}H^{8}O} + \underset{\text{Hydroxy-bibenzoic acid.}}{C^{14}H^{18}O^{5}}$$

(Otto, *Ann. Ch. Pharm.* cxxxiv. 303; *Jahresb.* 1865, p. 356.)—4. By passing a slow stream of dry hydrochloric acid gas through liquid sodium-amalgam covered with a layer of benzoyl chloride, $C^{7}H^{5}OCl$, this compound being thereby converted into benzoic aldehyde, and the latter, by further addition of hydrogen, into benzyl alcohol (Lippmann, *Bull. Soc. Chim.* [2] iv. 249).—5. By heating benzyl chloride with 3 pts. of recently precipitated lead oxide and 10 pts. water:

$$2C^{7}H^{7}Cl + PbH^{2}O^{2} = PbCl^{2} + 2C^{7}H^{8}O$$

(Lauth a. Grimaux, *ibid.* [2] vii. 105).

6. By the action of alcoholic potash on the portions of Peru-balsam oil boiling at 200°, and about the boiling point of mercury, the former consisting of benzyl benzoate, the latter of benzyl cinnamate. The benzyl alcohol thus obtained boils at 206·2° (corr.), has a sp. gr. of 1·0465 at 19°, and does not solidify at −18° (Kraut, *Ann. Ch. Pharm.* clii. 134).

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Paradichlorobenzyl alcohol, $C^{6}H^{3}Cl^{2}.CH^{2}OH$, is prepared by heating the corresponding acetate with ammonia to 180°, distilling the oily product to separate the more volatile portions, and recrystallising the portion which solidifies on cooling, from water. It forms white shining needles, very slightly soluble in water, melting at 77°, and partially decomposed by boiling.

Trichlorobenzyl alcohol, $C^{6}H^{2}Cl^{3}.CH^{2}OH$, is obtained by heating trichlorotoluene chloride, $C^{6}H^{2}Cl^{3}.CH^{2}Cl$, with potassium acetate to 150° in sealed tubes. The corresponding acetate is then formed, but decomposes partially on distilling the filtered solution, so that trichlorobenzyl alcohol distils over, and on mixing the distillate with water, separates as an oil, which solidifies after a while, and may be purified by recrystallisation from water. By oxidation with chromic acid, it is converted into trichlorobenzoic acid.

Tetrachlorobenzyl alcohol, $C^{6}HCl^{4}.CH^{2}OH$, is obtained by heating tetrachlorotoluene chloride, $C^{6}HCl^{4}.CH^{2}Cl$, with absolute alcohol and potassium acetate to 180°, and purified by crystallisation from boiling water.

Pentachlorobenzyl alcohol, $C^{6}Cl^{5}.CH^{2}OH$, prepared in like manner by heating $C^{6}Cl^{5}.CH^{2}Cl$ with absolute alcohol and potassium acetate to 200°, and purified by recrystallisation from a mixture of benzol and absolute alcohol, forms short white needles, melting at 193°, insoluble in water and in cold absolute alcohol, slightly soluble in boiling alcohol. It does not appear to yield any organic acid by oxidation with chromic acid.

Nitrobenzyl Alcohols. *Mononitrobenzyl alcohol*, $C^{6}H^{4}(NO^{2}).CH^{2}OH$, is produced, together with potassium nitrobenzoate, by heating nitrobenzoic aldehyde with alcoholic potash:

$$2C^{7}H^{5}(NO^{2})O + KHO = C^{7}H^{4}K(NO^{2})O^{2} + C^{7}H^{7}(NO^{2})O.$$

On adding water to the product, the nitrobenzyl alcohol separates as a viscid, uncrystallisable oil, which is decomposed by distillation under ordinary atmospheric pressure, but distils under a pressure of 3 millim. at 170°–180°, as an amber-coloured oil, which is converted by phosphorus pentachloride into a yellow chlorinated non-volatile liquid (Grimaux, *Bull. Soc. Chim.* [2] viii. 433).

Paranitrobenzyl alcohol, $C^{6}H^{4}(NO^{2}).CH^{2}OH$, is formed, together with acetamide, by heating paranitrobenzyl acetate with aqueous ammonia to 100°, till the oily layer disappears, and purified by recrystallisation from hot water. Colourless, slender needles, which become coloured on exposure to light, melt at 93°, dissolve easily in hot water or in water containing ammonia. Converted by oxidation into paranitrobenzoic acid (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2] iii. 467).

Paradinitrobenzyl alcohol, $C^{6}H^{3}(NO^{2})^{2}.CH^{2}OH$, formed by dissolving the preceding compound in fuming nitric acid, is precipitated from the solution by water, and crystallises in needles melting at 71° (Beilstein a. Kuhlberg, *loc. cit.*).

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Benzyl chloride. Chlorotoluene.

$$C^6H^4\left\{\begin{matrix} CH^2[CH^2(C^6H^5)] \\ H \end{matrix}\right. \qquad\qquad C^6H^4\left\{\begin{matrix} CH^3 \\ C^6H^4(CH^3). \end{matrix}\right.$$

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On adding water to the product, the nitrobenzyl alcohol separates as a viscid, uncrystallisable oil, which is decomposed by distillation under ordinary atmospheric pressure, but distils under a pressure of 3 millim. at 170°–180°, as an amber-coloured oil, which is converted by phosphorus pentachloride into a yellow chlorinated non-volatile liquid (Grimaux, *Bull. Soc. Chim.* [2] viii. 433).

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BENZYL OXYGEN-ETHERS. *Parachlorobenzyl acetate*, $C^6H^4Cl.CH^2(C^2H^3O^2)$, is prepared by prolonged boiling of a solution of chlorobenzyl chloride with a solution of potassium acetate in absolute alcohol, and rectifying the oil separated by water. Colourless aromatic liquid boiling at 240°. Converted by heating with ammonia into parachlorobenzyl alcohol (Neuhof, *Zeitschr. f. Chem.* [2] iii. 467). *Paradichlorobenzyl acetate*, $C^6H^3Cl^2.CH^2(C^2H^3O^2)$, prepared in like manner from dichlorobenzyl chloride, is an aromatic liquid boiling at 259° (Beilstein a. Kuhlberg).

Paranitrobenzyl acetate, $C^6H^4(NO^2).CH^2(C^2H^3O^2)$, is produced on dropping pure benzyl acetate (i. 21) into cooled fuming nitric acid. Separated by water and crystallised from alcohol, it forms long pale yellow needles, which become coloured on exposure to light, melt at 78°, dissolve sparingly in cold, freely in hot alcohol.

Parachlorobenzyl-ethyl oxide, $\left.\begin{matrix}C^7H^6Cl\\C^2H^5\end{matrix}\right\}O$, was obtained by Naquet (*Jahresb.* 1862, p. 420; 1863, p. 563) by decomposing chlorobenzyl chloride, $C^7H^6Cl.Cl$, with alcoholic potash, and is likewise formed by boiling parachlorobenzyl acetate with alcoholic potash. Heavy liquid, having an agreeably sweet odour, insoluble in water, boiling at 215°–220° (Beilstein a. Kuhlberg).

Benzyl oxalate, $(C^7H^7)^2C^2O^4$, produced by gently heating dry silver oxalate with an equivalent quantity of benzyl chloride, and purified by boiling the solidified product with alcohol, then melting, distilling, and recrystallising, forms dazzling white crystalline scales melting at 80·5°. It distils without decomposition, is insoluble in water, nearly insoluble in cold alcohol, but dissolves easily in boiling alcohol, also in ether and in benzol. With ammonia it yields benzyl alcohol and oxamide. *Paranitrobenzyl oxalate*, $[C^7H^6(NO^2)]^2C^2O^4$, is produced by dissolving benzyl oxalate in fuming nitric acid, and is decomposed by ammonia, with formation of paranitrobenzyl alcohol (Beilstein a. Kuhlberg, *loc. cit.*).

BENZYL SULPHYDRATE, SULPHIDE, and **BISULPHIDE.** The following reactions of these compounds have been observed by Märcker (*Ann. Ch. Pharm.* cxl. 86; *Jahresb.* 1866, p. 599), in addition to those already described (v. 858).

Benzyl sulphydrate mixed with an ethereal solution of *bromine*, till the colour of the latter disappears, is completely converted, with rapid evolution of hydrobromic acid, into benzyl bisulphide:

$$2C^7H^8S + Br^2 = 2HBr + (C^7H^7)^2S^2.$$

Metabenzyl sulphydrate is converted in like manner into metabenzyl bisulphide.

Benzyl sulphide, $(C^7H^7)^2S$, deliquesces in an atmosphere of *bromine* to a red-brown liquid, which strongly attacks the eyes, and consists of a mixture of sulphur bromide and benzyl bromide. *Benzyl bisulphide* is decomposed by bromine at 130°, and in presence of water benzoic acid is produced, together with a brown resin:

$$C^{14}H^{14}S^2 + 4H^2O + 5Br^2 = 2C^7H^6O^2 + 10HBr + S^2.$$

Ethyl-benzyl sulphide, $(C^2H^5)(C^7H^7)S$, is obtained by dissolving sodium in benzyl sulphydrate (mixed with ether to moderate the action), and treating the product with ethyl iodide. On adding water the ethyl-benzyl sulphide separates as an oil, which, after dehydration, may be distilled at 214°–216°, as a limpid liquid having an extremely pungent odour.

Benzyl-mercuric sulphide, $(C^7H^7)^2Hg''S^2$, heated to 130° with ethyl iodide, deliquesces to a lemon-yellow liquid, which solidifies to a crystalline mass on cooling.

BENZYL SULPHOCYANATE. $C^7H^7.CNS$.—When benzylamine is dissolved in carbon bisulphide, heat is evolved, and a colourless crystalline compound is formed, which, when mixed with alcohol and mercuric chloride, yields by distillation a liquid having a very powerful odour. On adding water to the alcoholic distillate, the benzyl sulphocyanate separates in transparent drops which sink in water. It smells like watercress and boils at 243° (Hofmann, *Zeitschr. f. Chem.* [2] iv. 690).

BENZYLAMINES. These bases, $(C^7H^7)H^2N$, $(C^7H^7)^2HN$, and $(C^7H^7)^3N$, discovered by Cannizzaro (i. 575; v. 867), have been further examined by Limpricht (*Ann. Ch. Pharm.* cxliv. 304; *Jahresb.* 1867, p. 508). They are formed by heating 1 vol. benzyl chloride (boiling at 170°–190°) and 2 vol. alcoholic ammonia to 100° for 24 hours, and separated by the different solubilities of their hydrochlorides in alcohol, the monobenzylamine salt being the most, and the tribenzylamine salt the least soluble. The crystalline pulp formed by heating the benzyl chloride with ammonia is freed from alcohol and ammonia by distillation, and then mixed with water; the resulting precipitate is dissolved in hot alcohol; and the solution mixed with hydrochloric acid is left to cool. Tribenzylamine hydrochloride then usually separates at first in prisms or needles, and the filtrate, after concentration, yields first a mixture of this salt with dibenzylamine hydrochloride, then pure crystals of the latter, and finally the hydrochloride of monobenzylamine, which is present in small quantity only.

Benzylamine, $(C^7H^7)H^2N = C^6H^5.CH^2NH^2$, is isomeric with *toluidine*. Separated from the hydrochloride by dilute caustic soda, it forms a transparent colourless liquid, which does not become coloured on exposure to light, has a faint peculiar odour, a sp. gr. of 0·990 at 14°, and boils at 183°. It dissolves in all proportions in water, alcohol, and ether, is separated from the aqueous solution by strong soda-ley, and when exposed to the air is quickly converted into *carbonate*. The *hydrochloride* and *hydrobromide* crystallise in easily soluble laminæ; the *platinochloride*, $2(C^7H^9N.HCl).PtCl^4$, is a yellow granular crystalline precipitate. With *fuming sulphuric acid*, benzylamine forms a sulpho-acid, whose calcium salt $(C^7H^8NSO^4)^2Ca$ is easily soluble in water, and separates on addition of alcohol in small warty crystals.

Dibenzylamine $C^{14}H^{15}N = (C^7H^7)^2HN = C^6H^5.CH^2NH(C^7H^7)$, separated from the hydrochloride by dilute soda-ley, is a colourless viscid liquid of sp. gr. 1·033 at 14°, insoluble in water, easily soluble in alcohol and ether, decomposing when heated, and easily converted into tribenzylamine by the action of benzyl chloride. The *hydrochloride*, $C^{14}H^{15}N.HCl$, crystallises in flat prisms or thin laminæ, melting at 250°; the *platinochloride*, $2(C^{14}H^{15}N.HCl).PtCl^4$, in orange-coloured concentrically grouped needles; the *hydrobromide*, $C^{14}H^{15}N.HBr$, in large nacreous laminæ, melting at 266°; the *hydriodide*, $C^{14}H^{15}N.HI$, in long white prisms melting at 224°; the *nitrate*, $C^{14}H^{15}N.HNO^3$, in somewhat sparingly soluble flat prisms or needles, melting at 186°. Dibenzylamine is converted into monobenzylamine by reactions exactly analogous to those by which it is itself produced from tribenzylamine (*vid. inf.*), but more slowly and less completely. With *fuming sulphuric acid*, dibenzylamine forms a non-crystallisable bibasic sulpho-acid, whose barium salt $C^{14}H^{13}NS^2O^6Ba$ crystallises in small nodular masses easily soluble in water. Dibenzylamine heated with *aniline* and *arsenic acid* yields an amorphous violet colouring matter.

Cyan-dibenzylamine, $C^{14}H^{14}(CN)N$, is formed, together with dibenzylamine hydrochloride, which separates out, when gaseous cyanogen chloride is passed into an alcoholic solution of dibenzylamine. It is insoluble in water, easily soluble in alcohol and ether, and separates therefrom in laminar crystals melting at 53°–54°.

Ethyl-dibenzylamine, $(C^7H^7)^2(C^2H^5)N$, is produced by heating dibenzylamine with ethyl iodide and alcohol to 110°, and is separated from its hydrochloride by silver oxide as a yellowish oil; the hydrochloride crystallises in nodular groups.

Tribenzylamine, $C^{21}H^{21}N = (C^7H^7)^3N = C^6H^5.CH^2N(C^7H^7)^2$, separated from the hot alcoholic solution of its hydrochloride by dilute soda-ley, and recrystallised from alcohol, forms large white laminæ or needles, easily soluble in ether and in hot alcohol, sparingly in cold alcohol, insoluble in water. It melts at 91°, may be distilled in small quantities without alteration; but in larger quantities it is decomposed, when heated above 300°, into toluene and several other products. The solution of tribenzylamine in *fuming sulphuric acid* contains a sulpho-acid (perhaps $C^{21}H^{21}NS^3O^9$), which appears to be resolved by water into two other acids, $C^{14}H^{15}NS^2O^6$ and $C^7H^8SO^4$, whose barium salts crystallise indistinctly and cannot be separated. Heated with *aniline* and *arsenic acid*, they yield an amorphous colouring matter which dissolves in alcohol or in hydrochloric acid with deep violet colour.

Tribenzylamine hydrochloride heated to 250° in a stream of hydrochloric acid gas is resolved into benzyl chloride and hydrochloride of dibenzylamine:

$$(C^7H^7)^3N.HCl + HCl = C^7H^7Cl + (C^7H^7)^2HN.HCl.$$

The *nitrate*, $(C^7H^7)^3N.HNO^3$, separates by spontaneous evaporation in transparent crystals melting at 124°. Tribenzylamine heated with *bromine* and *water* is resolved into hydrobromic acid, benzoic aldehyde, and hydrobromide of dibenzylamine:

$$(C^7H^7)^3N + Br^2 + H^2O = HBr + C^7H^6O + (C^7H^7)^2HN.HBr.$$

With *iodine* and *water* an analogous decomposition takes place at 120°. Dry *bromine* added to the ethereal solution of tribenzylamine throws down a yellow amorphous compound, $[(C^7H^7)^3N]^2Br^6$, which, when distilled with water, is resolved into benzoic aldehyde, dibenzylamine hydrobromide, hydrobromic acid, and free bromine.

Decomposition of Di- and Tri-benzylamine by Heat.—These bases, when slowly distilled in small retorts, yield a number of volatile products, together with a black-brown residue amounting to about half the original substance. The volatile products consist of ammonia, and a liquid which deposits crystals and yields by fractional distillation toluene, boiling at 112°. The crystalline deposit may be separated by repeated crystallisation from alcohol into dibenzyl, $C^{14}H^{14}$, toluylene, $C^{14}H^{12}$, and small quantities of crystalline azotised bodies. The black-brown residue of the distillate, when boiled with alcohol, yields lophine, $C^{21}H^{16}N^2$, in colourless silky needles. The same alcoholic extract mixed with hydrochloric acid deposits concentrically grouped quadratic prisms of tetrabenzylammonium chloride, $(C^7H^7)^4NCl$, and afterwards small white nodules of the hydrochloride of tribenzylene-triamine, $(C^7H^6)^3H^3N^3.HCl$ (Brunner, *Ann. Ch. Pharm.* cli. 133).

Chlorinated Benzylamines (Berlin, *ibid.* 137).—When chlorobenzyl chloride (p. 281) is heated in sealed tubes with alcoholic ammonia, there are formed, together with sal-ammoniac, the three bases $(C^7H^6Cl)H^2N$, $(C^7H^6Cl)^2HN$, and $(C^7H^6Cl)^3N$, the second being the most abundant. The separation of these bases is much more difficult than that of the three benzylamines (p. 336), partly because their salts differ but little in solubility, partly in consequence of the existence of isomeric modifications. The contents of the tubes were washed on a filter with alcohol; and the filtrate, after removal of the ammonia and the greater part of the alcohol by distillation with water, was mixed with the sal-ammoniac remaining on the filter, which still retained a considerable quantity of oil. The oily liquid thus obtained was a mixture of the three chlorinated bases with unaltered chlorobenzyl chloride. When mixed with alcohol and hydrochloric acid, it gradually deposited a considerable quantity (A) of the hydrochlorides of these bases, the crystallisation of the remainder being, however, prevented by the chlorobenzyl chloride still present. To complete the separation, the mother-liquor was mixed with potash; the precipitated oil distilled with water as long as chlorobenzyl chloride continued to pass over; and the residue, to facilitate the separation of the bases, was finally mixed with bromine, whereby the chlorotribenzylamine was resolved into chlorobenzoic aldehyde and dibenzylamine, the former passing over on distillation, and leaving a residue (B) consisting only of chlorinated mono- and di-benzylamine.

Chlorotribenzylamine. $(C^7H^6Cl)^3N$.—The oily mixture of the three bases (A) mixed with alcohol and hydrochloric acid first deposits the hydrochloride of chlorodibenzylamine, and the mother-liquor gradually yields transparent crystals of the hydrochloride of chlorotribenzylamine, from the alcoholic solution of which the base may be precipitated by potash and water. It crystallises from alcohol in beautiful rhombic prisms melting at 88°–89°. The *hydrochloride*, $(C^7H^6Cl)^3N.HCl + 2H^2O$, forms large transparent rhombohedrons, moderately soluble in alcohol, insoluble in water, melting at 170°–175°, giving off part of their water on exposure to the air, and the whole over sulphuric acid. At 100° they decompose, apparently thus:

$$(C^7H^6Cl)^3N.HCl = \underset{\text{Chlorodibenzylamine.}}{(C^7H^6Cl)^2HN} + \underset{\text{Chlorobenzyl chloride.}}{C^7H^6Cl^2}$$

The same decomposition appears to takes place on distilling the hydrochloride with water or alcohol; and hence it is that, in the preparation of these bases, the residue left after distilling off the alcohol contains only a small quantity of chlorotribenzylamine, but considerable quantities of chlorodibenzylamine and chlorobenzyl chloride. Chlorotribenzylamine is resolved by distillation with water and bromine into hydrobromide of chlorodibenzylamine and chlorobenzoic aldehyde:

$$(C^7H^6Cl)^3N + H^2O + Br^2 = (C^7H^6Cl)^2HN.HBr + C^7H^5ClO + HBr.$$

Chlorodibenzylamine. $(C^7H^6Cl)^2HN$.—This base exhibits four isomeric modifications, which may be distinguished by the prefixes α, β, γ, δ. They are non-volatile oils, having a faint yellowish colour, insoluble in water, easily soluble in alcohol and ether. The differences between them are exhibited chiefly in their salts. The hydrobromides differ in solubility sufficiently to admit of separation by fractional crystallisation, the α salt being the least soluble, then the β, then the γ, and the δ salt the most soluble in water; and from these salts the bases may be separated by potash and combined with other acids. Most of the salts crystallise in needles. Their melting points are given in the following table:

	α	β	γ	δ
Hydrochlorides . .	288°–289°	225°–228°	218°–220°	221°–222°
Hydrobromides . .	283°–290°	224° (solidifying at 230°)	210°–212°	198°–199°
Hydriodides		215°	187°	216°–218°
Nitrates		204°–205°	193°	177°–179°

Chlorobenzylamine. $(C^7H^6Cl)H^2N$.—The hydrobromide of this base remains in the mother-liquor of the mixture B after the chlorodibenzylamine salt has crystallised out. By distilling it with potash, the base is obtained as a colourless liquid, easily soluble in alcohol and ether, insoluble in water, and converted into a solid salt by absorption of carbonic acid from the air. The *hydrochloride* $(C^7H^6Cl)H^2N.HCl$ forms small white needles easily soluble in water and in alcohol and melting at 197°. Platinic chloride forms in the concentrated alcoholic solution a yellow precipitate formed of microscopic rhombic laminæ moderately soluble in water and in alcohol.

BENZYLENE. C^7H^6.—The bromide and chloride of this diatomic radicle, together with the substitution-derivatives of the latter, $C^7H^5Cl.Cl^2$, $C^7H^4Cl^2.Cl^2$, &c., are described amongst the bromo- and chloro-toluenes (pp. 281, 282). The oxygen-ethers of the same radicle are described in vol. i. pp. 577, 578.

BENZYL-SULPHUROUS ACID. Syn. with TOLUENE-SULPHURIC or SULPHO-TOLUIC ACID (v. 553, and p. 286 of this volume).

BERBERINE. $C^{20}H^{17}NO^4$ (i. 579 and APPENDIX v. 1088).—This base has been found in *Leontice thalictroïdes* (F. F. Mayer, *J. Pharm.* [3] xlvi. 496). According to Daniel (*Ann. Ch. Pharm.* cv. 360), the yellow bark of Abeocouta, in which Stenhouse found berberine, belongs to *Cælocline polycarpa* (Dec.). Berberine is identical with xanthopicrine from *Xanthoxylon Clava Herculis*, and with jamaïcine from the bark of *Geoffroyea inermis* (Gastell, *Jahresb.* 1866, p. 480).

Preparation.—The following method is given by Stenhouse (*Chem. Soc. J.* [2] v. 187) for preparing berberine from the columbo-wood of Ceylon (*Menispermum fenestratum, Coscinium fenestratum*): 20 pts. of the finely ground wood are boiled for three hours with a solution of basic lead acetate (prepared by heating 1 pt. of the neutral acetate with 1 pt. litharge and 3 pts. water, and afterwards adding 100 pts. water), and the liquid, strained through a linen filter, is concentrated (with addition of a little litharge) till the berberine crystallises out. The mother-liquor decanted from the crystals and acidulated with nitric acid yields the rest of the base, as a nitrate slightly soluble in the excess of acid. To purify the crude berberine, the hot aqueous solution is precipitated with basic lead acetate; the crystalline mass which separates from the filtrate on cooling is pressed, and redissolved in hot water; and, after the lead has been precipitated by hydrogen sulphide, the filtrate is acidulated with acetic acid and left to crystallise. The nitrate may be converted into the free base by heating its aqueous solution with ammonia, or better with calcium hydrate.

Procter (*Chem. News*, ix. 112) recommends a process given by W. A. Merril (*Am. J. Pharm.* xxxv. 97) for preparing berberine from the root of *Berberis vulgaris* or of *Hydrastis canadensis*. The evaporated aqueous extract of the root is treated with strong alcohol; the alcoholic liquid mixed with $\frac{1}{4}$ vol. water; $\frac{5}{8}$ of the alcohol distilled off; and the hot aqueous residue acidulated with dilute sulphuric acid. On cooling, it deposits berberine sulphate, which may be purified by recrystallisation. To obtain the free base, the hot aqueous solution of the sulphate is digested with recently precipitated lead oxide till the supernatant liquid is free from sulphuric acid. The filtrate left to evaporate deposits crystals of berberine.

Reactions.—Berberine heated with *water* to 190°–200° for several days in sealed tubes is gradually converted into a substance resembling chlorophyll (Hlasiwetz, *Jahresb.* 1860, p. 533). By nascent hydrogen (zinc and dilute acids), it is converted into hydroberberine, $C^{20}H^{21}NO^4$ (iii. 185). By fusion with *potassium hydrate*, berberine is converted into two acids, $C^8H^8O^4$ and $C^9H^8O^5$ (?), the former homologous with protocatechuic, the latter probably with opianic acid (Hlasiwetz a. Gilm, *Jahresb.* 1864, p. 406). Berberine distilled with *sodium hypochlorite*, yields propylamine (? trimethylamine), and a yellow resinous substance not containing nitrogen (Kletzinsky, *ibid.* 1865, p. 456).

An aqueous solution of berberine acetate forms with *sodium sulpharsenate*, a brown amorphous precipitate which decomposes in a few days (Mosing, *Zeitschr. f. Chem.* [2] v. 350).

The salts of berberine have been analysed by Fleitmann (*Ann. Ch. Pharm.* lix. 160), L. Henry (*ibid.* cxv. 132), and Perrins (*Chem. Soc. J.* xv. 339). The formulæ, calculated by Fleitmann and Henry according to the old formula of berberine, have been corrected by Hlasiwetz a. Gilm (*Ann. Ch. Pharm. Suppl.* ii. 191).

Hydrochloride,	$C^{20}H^{17}NO^4.HCl$,	yellow needles.
Aurochloride,	$C^{20}H^{17}NO^4.HCl.AuCl^3$,	maroon-coloured needles soluble in alcohol.
Platinochloride,	$2(C^{20}H^{17}NO^4.HCl).PtCl^4$,	small needles.
Hydrobromide,	$C^{20}H^{17}NO^4.HBr.3aq.$,	yellow needles.
Hydriodide,	$C^{20}H^{17}NO^4.HI$,	yellow, slightly soluble needles.

Nitrate,	$C^{20}H^{17}NO^4.HNO^3$,	yellow, very slightly soluble in dilute nitric acid.
Chlorate,	$C^{20}H^{17}NO^4.HClO^3$,	yellow precipitate.
Sulphate,	$C^{20}H^{17}NO^4.H^2SO^4$,	small yellow crystals.
Argento-berberine Hyposulphite,	$(C^{20}H^{17}NO^4)^2.H^2S^2O^2.Ag^2S^2O^3$,	yellow amorphous precipitate.
Dichromate,	$\begin{matrix}CrO^2\\CrO^2\end{matrix}\left\{\begin{matrix}OHC^{20}H^{17}NO^4\\O\\OHC^{20}H^{17}NO^4\end{matrix}\right.$,	orange-yellow needles.
Hydrocyanide,	$C^{20}H^{17}NO^4.CNH.\frac{1}{2}aq.$,	brownish-yellow scales.
Nitro-berberine Hydrocyanide,	$C^{20}H^{16}(NO^2)NO^4.CNH$,	microscopic needles.
Sulphocyanate,	$C^{20}H^{17}NO^4.CNHS.\frac{3}{2}aq.$,	yellow needles.
Oxalate,	$C^{20}H^{17}NO^4.C^2H^2O^4.\frac{1}{2}aq.$,	nodular groups of needles.
Succinate,	$C^{20}H^{17}NO^4.C^4H^6O^4.\frac{1}{2}aq.$,	brownish needles.
Tartrate,	$C^{20}H^{17}NO^4.C^4H^6O^6.\frac{1}{2}aq.$,	siskin-yellow needles.
Picrate,	$C^{20}H^{17}NO^4.C^6H^2(NO^2)^3O$,	golden-yellow shining scales.
Ethyl-berberine Hydriodide,	$C^{20}H^{16}(C^2H^5)HO^4.HI$,	radiate needles.

Tartrate of Antimony and Berberine, $C^{20}H^{17}NO^4.HSbO.C^4H^4O^6$, crystallises in wavellitic groups, very slightly soluble in cold water, and recrystallisable without decomposition from alcohol (Stenhouse, *Proc. Roy. Soc.* xii. 491).

A solution of a berberine salt mixed with a slight excess of iodine yields the *periodide* $C^{20}H^{17}NO^4.HI^3$, which dissolves but sparingly in water and in cold alcohol, and crystallises from hot alcohol in translucent red-brown prisms, from which silver nitrate immediately abstracts the whole of the iodine. A hot alcoholic solution of a berberine salt mixed with a dilute solution of iodine in potassium iodide, carefully avoiding excess of iodine, deposits green shining spangles of a salt resembling sulphate of iodoquinine (v. 25), and exhibiting the peculiar polarising properties of that compound; they are always, however, mixed with the salt last described, and with berberine hydriodide. The formation of this green salt affords a very delicate test for the presence of berberine. It may be obtained in crystals $\frac{1}{4}$ inch long and half as broad by heating a solution of berberine in 90 p. c. alcohol mixed with ethyl iodide to 100°, leaving it to cool, and exposing the separated crystals of berberine hydriodide to the sun's rays for two hours, or to diffused daylight for a few days. It is probably identical in composition with the red salt, into which, indeed, it is very easily transformed (Perrins).

BENZELIANITE. This mineral, occurring at Skrikerum in Sweden, as a black-blue crystalline powder of sp. gr. 6·71, has been analysed by A. Nordenskjöld (*Ann. Ch. Pharm.* cxlv. 127), with the following results:

Cu	Ag	Fe	Fl	Se
53·14	4·73	0·54	0·38	39·85 = 98·64,
52·15	8·50	0·35	trace	38·74 = 99·74.

BETAINE. $C^5H^{11}NO^2$ (C. Scheibler, *Zeitschr. f. Chem.* [2] v. 539).—A base occurring in the juice of mangold-wurzel. To prepare it, the freshly expressed juice, strongly acidulated with hydrochloric acid, is mixed with a solution of sodium phosphotungstate;* the resulting precipitate, containing albumin, colouring matter, woody fibre, and a small quantity of the base, is filtered as quickly as possible; and the filtrate, mixed with a fresh quantity of the precipitant, is left to itself for 8 or 10 days. It then gradually deposits on the bottom and sides of the vessel a crystalline precipitate, which is rinsed with a little water and treated with milk of lime, whereby insoluble calcium phosphotungstate is produced, while the betaine remains in solution. The filtered liquid, freed from lime by carbonic acid and evaporated, leaves impure betaine, which may be purified by recrystallisation from alcohol with help of animal charcoal.

Betaine may also be obtained from the molasses of the beet, in which it exists in larger proportion than in the fresh juice. The solution of the molasses, diluted with twice its bulk of water, and strongly acidulated with hydrochloric acid, is mixed with a small quantity of the phosphotungstate solution, which throws down chiefly colouring matter and impurities, and the filtrate is mixed with a larger quantity of the same reagent, which throws down a second precipitate, to be treated as above.

Betaine crystallises from strong alcohol in large shining hydrated crystals,

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* This reagent is prepared by dissolving sodium bitungstate in ordinary phosphoric acid, adding hydrochloric acid, and decanting the clear solution from the precipitate thereby produced.

$C^5H^{11}NO^2.H^2O$, which on exposure to the air quickly deliquesce to a colourless syrup. At 100°, or over sulphuric acid, they effloresce and give off all their water. They are extremely soluble in water; a solution saturated at 25° has a sp. gr. of 1·1177, and contains 61·8 p. c. of the anhydrous base. Betaine is inodorous, has a sweetish cooling taste, is neutral to vegetable colours, and optically inactive. When heated it swells up, emitting an odour first of trimethylamine, then of burnt sugar, and leaves a bulky cinder, which burns away slowly but completely.

Betaine hydrochloride, $C^5H^{11}NO^2.HCl$, and the *sulphate*, form splendid crystals permanent in the air; the *nitrate* crystallises in deliquescent needles. The *aurochloride*, $C^5H^{11}NO^2.HCl.AuCl^3$, crystallises in beautiful thin needles or plates, sparingly soluble in cold, easily in hot water. With *platinic chloride*, betaine hydrochloride forms two compounds, which perhaps differ from one another only in their amount of crystallisation-water. It also forms well-crystallised double salts with the chlorides of mercury, cadmium, and zinc.

Betaine is not oxidised by chromic acid, or reduced by hydriodic acid, even when heated with it in sealed tubes. When boiled with potassium hydrate and a small quantity of water, it gives off trimethylamine, and forms at least two fixed bases, one of which yields an aurochloride containing $C^8H^{17}NO^3.HCl.AuCl^3$.

Betaine is isomeric or polymeric with trimethylated glycollamide, with butalanine, lactamethane, &c., also with oxyneurine.

BEUSTITE. A shining mineral, containing lime, potash, and soda, from Mount Sforzella, near Predazzo. Sp. gr. 2·18 (Breithaupt, *Jahresb.* 1863, p. 846).

BILE. In applying Pettenkofer's test for bile (i. 586), the following method is recommended by J. Neukomm (*Ann. Ch. Pharm.* cxvi. 30; *Jahresb.* 1862, p. 584), as affording the most delicate indications. The biliary acids are precipitated with basic lead acetate; the washed precipitate is mixed with sodium carbonate and evaporated to dryness; the sodium salts of the biliary acids are dissolved out by absolute alcohol; the residue left on evaporating the alcoholic solution is dissolved in water; and a drop of the aqueous solution is mixed in a porcelain capsule with a drop of dilute sulphuric acid (4 pts. water to 1 pt. of the concentrated acid) and a very small quantity of sugar solution. On evaporating the solution at a gentle heat, a splendid purple-violet coloration is obtained, even with only 0·06 milligrm. of biliary acids; 0·005 grm. cholic acid may in this manner be detected with certainty in a litre of water; in the same quantity of liquid, 0·01 grm. glycocholic acid gives only a faint, 0·02 grm. a deep purple-red coloration.

In applying the test to the detection of bile in urine, it is necessary to remove the inorganic salts as completely as possible before precipitating with basic lead acetate. For this purpose, the urine, evaporated to a thick syrup, is treated with alcohol of ordinary strength; the residue left on evaporating the solution is exhausted with absolute alcohol; the evaporated residue, which now contains but a small quantity of inorganic salts, is dissolved in a little water; the solution is precipitated with basic lead acetate; and the precipitate is collected after twelve hours. To remove other substances still adhering to the lead precipitate, it is digested with boiling alcohol, and the residue is converted into sodium salt. If the latter, as sometimes happens, still contains a small quantity of resinous substance, which would mask the reaction with sulphuric acid and sugar, its aqueous solution must be again precipitated with basic lead acetate, and the lead precipitate reconverted into sodium salt. In this manner, a quantity of glycocholic acid not exceeding 0·001 p. c. may be detected in urine (Neukomm).

Huppert (*Jahresb.* 1867, p. 880) points out that the indications of Pettenkofer's bile test may be masked by the presence of oxidising substances, such as nitrates and chlorates. It is scarcely necessary, however, to observe that such salts could not be present in the lead precipitate obtained as above.

Noel (*J. Pharm.* [3] xli. 354) recommends, as a test for bile, to immerse a strip of filtering paper for a few minutes in the liquid, then dry it, and moisten it with a drop of nitric acid, either pure or containing nitrous acid: it will then assume a violet colour, changing to red and yellow.

The biliary acids and their products of decomposition are optically dextrogyrate. Their rotatory powers, as determined by Hoppe-Seyler (*J. pr. Chem.* lxxxix. 257; *Bull. Soc. Chim.* v. 622), are given in the following table:

Optical Rotatory Power of Bile-constituents	Formula	Molecular Weight m	Specific Rotation for the line D (α) D	Molecular Rotatory Power (α) D m	$(\alpha)\mathrm{D}\frac{m}{408}$
a. **Dissolved in Alcohol:**					
Sodium Glycocholate .	$C^{26}H^{42}NO^{6}Na$	487	25·7°	12516	31·5°
Sodium Taurocholate .	$C^{26}H^{44}NSO^{7}Na$	537	24·5	13157	31·9
Glycocholic Acid . . .	$C^{26}H^{43}NO^{6}$	465	29·0	13485	33·0
Sodium Cholate	$C^{24}H^{39}O^{5}Na$	430	31·4	13502	33·1
Potassium Cholate . .	$C^{24}H^{39}O^{5}K$	446·2	30·8	13743	33·7
Methyl Cholate	$C^{24}H^{39}O^{5}.CH^{3}$	422	31·9	13462	33·0
Ethyl Cholate	$C^{24}H^{39}O^{5}.C^{2}H^{5}$	436	32·4	14126	34·7
Cholic Acid + aq. . .	$C^{24}H^{40}O^{5}.\frac{5}{2}H^{2}O$	447	31·2	13946	34·7
Cholic Acid	$C^{24}H^{40}O^{5}$	408	50·2	20482	50·2
b. **Dissolved in Water:**					
Sodium Glycocholate .	$C^{26}H^{42}NO^{6}Na$	487	20·8	10130	24·8
Sodium Taurocholate .	$C^{26}H^{44}NSO^{7}Na$	537	21·5	11546	28·2
Potassium Cholate . .	$C^{24}H^{39}O^{5}K$	446·2	25·0	11151	27·3
Sodium Cholate	$C^{24}H^{39}O^{5}Na$	430	26·0	11188	27·4

The expression $(\alpha)\ \mathrm{D}\frac{m}{408}$ gives the value of the rotation reduced to the (active) atomic group of cholic acid, $C^{24}H^{40}O^{5}$, which exists in all these bile-constituents and determines the dextro-gyration. From the last two columns of the table, it appears that the highest molecular rotatory power is exhibited by cholic acid, and that in general the rotation diminishes as the complexity of the molecule increases, although the decrease does not bear any definite proportion to the increase of molecular weight. As the rotatory power of the several substances is less in aqueous than in alcoholic solution, it may be concluded that the water exerts a chemical action upon them, resulting in an increase of molecular weight. The differences of rotatory power of the several groups of atoms do not (excepting in the case of anhydrous cholic acid) exceed 3°, that is to say, about $\frac{1}{10}$ of the total rotation.

The optical rotatory power of the bile-constituents may be made available for verifying the analysis of a mixture of glycocholic and taurocholic acids, such as exists in the bile of man and of vegetable-feeders. The mixture (after precipitation from alcohol by ether) is dissolved in alcohol; the rotation is determined for yellow light; a measured volume of the solution, not too small, is evaporated; and the residue, dried at 120° and weighed, is heated to 100° with strong potash-ley in a glass tube for twenty-four to thirty hours. The contents of the tube (containing all the cholic acid that can be formed as product of decomposition) are mixed with a little ether and hydrochloric acid; the separated cholic acid is collected after twenty-four hours on a filter, washed with water, and redissolved in hot alcohol; and the evaporated residue is weighed after drying at 120°. In the liquid filtered from the cholic acid the sulphur is determined by fusion with carbonate and nitrate of potassium. Since 100 pts. barium sulphate correspond to 220·8 pts. taurocholic acid, $C^{26}H^{45}NSO^{7}$, and 100 pts. of the latter to 79·2 pts. cholic acid, $C^{24}H^{40}O^{5}$, the amount of taurocholic acid present in the mixture may be calculated, also the quantity of cholic acid produced therefrom, and (since 100 pts. cholic acid correspond to 113·9 pts. glycocholic acid) likewise the amount of glycocholic acid present. The correctness of these estimations may be tested by the rotatory power of the mixture. If the observed rotation in degrees for yellow light in a tube 1 decim. long be denoted by α, and the calculated quantity of taurocholic acid in the liquid by m, then, since the specific rotation of taurocholic acid (as sodium salt in alcoholic solution) is 25·3°, and that of glycocholic acid under similar circumstances = 27·6 for yellow light, the quantity of glycocholic acid is $\frac{100\,\alpha - 25{\cdot}3\,m}{27{\cdot}6}$. If the rotation gives a lower value than the cholic acid estimation, the presence of inactive fatty acids may be inferred; if, on the other hand, the value is too high, cholic acid itself must have been present. An examination of dog's bile by this method showed, in accordance with Strecker's results, that this bile contains only taurocholic acid (Hoppe-Seyler, *J. pr. Chem.* lxxxix. 221; *Jahresb.* 1863, p. 717).

For Fröhde's view of the origin of the biliary acids, see *Zeitschr. Ch. Pharm.* 1864, p. 464; *Jahresb.* 1864, p. 656.

Pig-bile contains—besides fats and cholesterin—a non-soluble substance, lecithin, resolvable by baryta-water into glycerophosphoric acid and fatty acids (iii. 566); also sarcolactic acid and choline, $C^5H^{15}NO$. This base is also contained in the bile of the ox, and probably also in that of many other animals (Strecker, *Rép. Chim. pure*, iii. 345; *Ann. Ch. Pharm.* cxxiii. 353). See CHOLINE. According to J. Dogiel (*J. pr. Chem.* ci. 298), fresh ox-bile contains acetic and propionic acids, partly as metallic salts, partly as glycerides.

Goose-bile contains, according to R. Otto (*Zeitschr. f. Chem.* [2] iv. 633), 3·1 p. c. mucus, 0·3 fat, cholesterin, and colouring matter, 19·0 biliary acids and inorganic salts, and 77·6 water. Otto has confirmed the results obtained by Marrson and by Heintz a. Wislicenus, to the effect that the sulphuretted acid of goose-bile, taurochenocholic acid, differs in composition from the taurocholic acid of human bile, dog-bile, &c. Otto finds that the sodium salt of taurochenocholic acid, dried at 100°–110°, has the composition $C^{29}H^{50}NaNSO^7$, or rather $C^{29}H^{48}NaNSO^7.H^2O$, and gives off a molecule of water at 140°, leaving the anhydrous salt $C^{29}H^{48}NaNSO^6$, whence the acid has the constitution $C^{29}H^{49}NSO^6$*, and is resolved by boiling with baryta-water into taurine and chenocholic acid:

$$C^{29}H^{49}NSO^6 + H^2O = C^2H^7NSO^3 + C^{27}H^{44}O^4.$$

Goose-bile appears also to contain another sulphuretted acid, less soluble in water than taurochenocholic acid, and crystallising in small nacreous scales; but it has not been obtained pure. No acid analogous to glycocholic acid has yet been found in goose-bile.

The bile of the horn-fish (*Bellone vulgaris*), like that of other fresh-water fish (i. 686), consists essentially of sodium taurocholate (Otto, *Ann. Ch. Pharm.* cxlv. 352).

Bile-constituents in Excrementitious Matters.—Cow-dung contains cholic and glycocholic acids; that of the dog contains cholic acid; pigeons' dung also contains a biliary substance. Peruvian guano contains a not inconsiderable quantity of an uncrystallisable, optically inactive biliary acid, insoluble in water, easily soluble in alkalis, and converted by boiling with concentrated hydrochloric acid into products analogous to choloidic acid and dyslysin, dissolving in strong sulphuric acid, and forming green fluorescent solutions, which, like the original acid, give the purple-violet coloration with sulphuric acid and sugar. The acid does not contain sulphur, and is probably also free from nitrogen. Peruvian guano also contains cholesterin, but no bile-pigments (Hoppe-Seyler, *Jahresb.* 1863, p. 654).

BILE-PIGMENTS. The colouring matters of bile are described in the article CHOLOCHROME (i. 927) chiefly according to the results obtained by Thudichum in 1860. Since that time they have been further examined by several chemists, whose results, though differing in minor details, agree in showing that the brown and green pigments of bile may be separated by means of chloroform, in which the former is soluble, the latter insoluble, and that the pigment soluble in chloroform exhibits two modifications, one red (*bilirubin*), the other brown (*biliphæin* or *colophæin*).

When bile is shaken up with chloroform, and the chloroform separated and evaporated, a crystalline substance is obtained, which, after washing with alcohol and ether, remains as a brick-red powder, soluble in ammonia; and the ammoniacal solution mixed with hydrochloric acid yields yellowish-brown flocks of cholophaein (E. Brücke, *J. pr. Chem.* lxxvii. 72; *Jahresb.* 1859, p. 637).

Thudichum (*Zeitschr. f. Chem.* [2] iv. 554) prepares bilirubin and cholophæin from gall-stones, by exhausting the pulverised calculi with hot water, alcohol, and cold dilute hydrochloric acid in succession, then again with alcohol; boiling the dried powder with water and chloroform free from hydrochloric acid; and mixing the concentrated dark green solution thereby obtained with alcohol. Bilirubin is then precipitated of a red colour as bright as that of mercuric oxide, and the mother-liquor yields brown rhombic crystals of cholophaein. The red and brown pigments thus obtained are identical in composition, and are represented by the formula $C^9H^9NO^2$. The red modification may be converted into the brown by repeated crystallisation. The red (or brown) pigment is insoluble in water, nearly insoluble in boiling alcohol and in ether, more soluble in benzol and carbon bisulphide, still more in chloroform (1 pt. in 586). When the chloroform solution is exposed to sunshine, the colouring matter is decomposed, probably owing to the formation of hydrochloric acid. Saturated aqueous *ammonia* converts bilirubin into a dark red bulky mass, probably $C^9H^8(NH^4)NO^2.H^2O$, which gives off all its ammonia in a stream of dry air. Bilirubin dissolves in dilute ammonia, and is reprecipitated unaltered by hydrochloric acid. It dissolves in the *fixed caustic alkalis* with brown-red colour, and the solution, if immediately mixed with hydrochloric acid, deposits brown flocks which redissolve in chloroform; but on exposing the alkaline solution to the air, biliverdin is produced. The potassium and sodium compounds of bilirubin are insoluble in chloroform. A neutral ammoniacal solution of cholophæin, obtained by digesting the pigment with weak aqueous ammonia, yields with *silver nitrate* a red-brown precipitate of the compound $C^9H^{10}AgNO^3$ (or perhaps $C^9H^8AgNO^2.H^2O$); but if the solution contains excess of ammonia, it yields, on addition of silver nitrate and subsequent neutralisation with nitric acid, a precipitate of the diargentic salt $C^9H^7Ag^2NO^2$. In an ammoniacal solution of the pigment containing excess of ammonia, *barium chloride* forms a precipitate containing $(C^9H^{10}NO^3)^2Ba$ (at 100°); but a neutral solution yields a precipitate containing excess of bilirubin; *calcium chloride* yields similar precipitates. *Neutral lead acetate* added in excess to an ammoniacal solution of bilirubin forms a precipitate consisting of $C^9H^7PbNO^2$ (Thudichum). See also Maly (*Zeitschr. f. Chem.* [2] v. 394), who, however, assigns to the red or brown pigment (which he calls *cholepyrrhin*) the formula $C^{16}H^{18}N^2O^3$.

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* In the formula of taurochenocholic acid given at p. 700, vol. v., there is a misprint of O^7 for O^6.

Städeler (*Ann. Ch. Pharm.* cxxxii. 323; *Jahresb.* 1864, p. 657) has also examined the colouring matters of bile, but with somewhat different results. By exhausting strongly coloured pulverised gall-stones with ether, hot water, chloroform, and dilute hydrochloric acid, he obtains a brownish-green residue, from which boiling chloroform extracts a brown pigment (*bilifuscin*), together with a portion of the red pigment (*bilirubin*), whilst the undissolved portion yields to alcohol a green pigment (*biliprasin*), and then to hot chloroform the rest of the bilirubin. Städeler represents bilirubin by the formula $C^{16}H^{18}N^2O^3$, bilifuscin by $C^{16}H^{20}N^2O^4$ (bilirubin + H^2O), and biliprasin by $C^{16}H^{22}N^2O^6$. The residue left after exhausting the gall-stones successively with water, alcohol, ether, chloroform, and dilute acid, and forming a considerable portion of the whole, is a humus-like substance, designated by Städeler as *bilihumin* [? impure biliverdin]; it has not been analysed.

Biliverdin or ***Cholochlorin*** is formed when an alkaline solution of bilirubin is exposed to the air; the oxidation may be accelerated by passing a current of air through the heated liquid. The green solution thus formed yields with hydrochloric acid, green flocks, which appear black when dry, are quite amorphous, insoluble in water, ether, and chloroform, but easily soluble in alcohol (Thudichum); easily soluble in benzol and carbon bisulphide, very slightly soluble in amyl alcohol and ethyl iodide, but easily soluble in these last-mentioned liquids on addition of ethylic or methylic alcohol (Maly).

Biliverdin consists, according to Thudichum, of $C^8H^9NO^2$, and is formed from bilirubin in the manner represented by the equation:

$$C^9H^9NO^2 + O^3 = C^8H^9NO^2 + CO^2.$$

Städeler, on the other hand, represents it by the formula $C^{16}H^{20}N^2O^5$ [$= 2C^8H^9NO^2 + H^2O$], and finds that it may be formed by boiling an alkaline solution of bilirubin even when the access of air is completely prevented. He represents its formation by the first or second of the following equations, accordingly as the air has access to the solution or not:

$$\underset{\text{Bilirubin.}}{C^{16}H^{18}N^2O^3} + H^2O + O = \underset{\text{Biliverdin.}}{C^{16}H^{20}N^2O^5}$$

$$\underset{\text{Bilirubin.}}{C^{16}H^{18}N^2O^3} + 2H^2O = \underset{\text{Biliverdin.}}{C^{16}H^{20}N^2O^5} + C^{16}H^{20}N^2O^3.$$

The latter equation supposes the simultaneous formation of a second body, perhaps identical with that which is formed from biliverdin by reduction with sodium-amalgam.

Biliverdin dissolves in potash, soda, and ammonia, and is not precipitated from the solutions of calcium or barium chloride: but in alcoholic solution it forms dark green precipitates with *baryta-water*, *lime-water*, and with the *acetates of lead*, *mercury*, and *silver*. The barium and calcium compounds are soluble in water, the rest insoluble (Thudichum; Maly).

Reducing agents, such as hydrogen sulphide, zinc in acid solution, and sodium-amalgam, act upon biliverdin, but do not reconvert it into bilirubin. With *iodine* and *chlorine* it forms resinous products An alcoholic solution of biliverdin treated with *silver oxide* forms a purple compound, bilipurpin, which, however, remains combined with the silver oxide, forming a compound which dissolves in ammonia, and yields bilipurpin on adding hydrochloric acid to the solution. The presence of bile-pigments may accordingly be detected by boiling the substance under examination with an ammoniacal solution of silver oxide, and acidulating the filtrate with hydrochloric acid, whereupon, if bile-pigments are present, even in very small quantity, a purple colour will be produced. By prolonged action of silver-oxide, bilipurpin is converted into a yellow substance, biliflavin. Mercuric oxide does not act perceptibly on biliverdin; peroxides act like silver oxide. The alcoholic solution of biliverdin gradually mixed with *nitric acid* assumes a bluish-violet, then red, and ultimately yellow colour (Thudichum).

These colours, which are also produced by the action of nitric acid on crude bile-pigment,* correspond, according to Jaffe (*Zeitschr. f. Chem.* [2] v. 666), to characteristic alterations of the spectrum. The blue-violet solution exhibits in the spectrum a broad absorption-band between the lines C and D, which on dilution is resolved into two bands (α and β) separated by a bright band near D. Another absorption-band, γ, occurs between the lines *b* and F. As the action of the nitric acid progresses, the bands α and β gradually disappear, while γ becomes more distinct, and when the solution exhibits a red colour, γ likewise disappears.

The pigment contained in the blue-violet solution above mentioned may be obtained in the separate state by treating an alcoholic solution of biliverdin, or an ammoniacal solution of bilirubin mixed with alcohol, with a mixture of ordinary concentrated nitric acid and the fuming acid, till a sample exhibits the absorption-bands α and β, then mixing the solution with chloroform, and shaking it up with water. The water is then removed; the chloroform layer containing the blue pigment is filtered from biliverdin, and evaporated to dryness; and the residue is purified by repeated solution in chloroform. The substance thus obtained is of a deep violet colour, insoluble in water, easily soluble in alcohol, ether, and chloroform, forming violet solutions. Alkalis dissolve it with brown-violet colour; acids with a fine blue colour. The neutral and alkaline solutions exhibit no absorption-bands; but the smallest trace of acid brings to light the bands α, β, and γ. The blue pigment dissolves in strong sulphuric acid, forming a dark green solution, which on addition of water deposits green flocks. The liquid filtered from these flocks is blue by reflected, violet by transmitted light, becomes brown when mixed with sodium carbonate, and is not decolorised by glucose: hence it does not contain indigo. If in the preparation of the blue substance the action of the nitric acid has been carried too far, the acid solutions have a violet colour. On agitating the sulphuric acid solution with ether, the latter becomes red, and the acid liquid again blue.

The pigment corresponding to the absorption-band γ may be obtained in exactly the same way as the blue pigment, excepting that the action of the nitric acid must be carried so far as to cause the bands α and β to disappear completely. The substance thus obtained is brown-red, and dissolves in alcohol, ether, and chloroform with a fine red colour, not altered by alkalis or acids. It is only the acid solution that exhibits the band γ (Jaffe).

When human bile or dog-bile is treated with hydrochloric acid, a red solution is obtained which exhibits very distinctly the absorption-band γ. On adding an alkali the solution acquires a yellow colour (least distinct with ammonia), and then exhibits an absorption-band δ, also between C and F, but nearer to C. The colouring matter may be extracted from the solution by chloroform, and on evaporating the latter, there remains a red residue, which is soluble in water, alcohol, and chloroform, and is precipitated from the aqueous solution by lead acetate or calcium chloride. The same red pigment is found in normal human urine (Jaffe).

A solution of cholophæin in chloroform obliterates the entire blue and violet end of the spectrum as far as the line 70 of Bunsen's scale. Very dilute but still yellow solutions absorb only the violet. Solutions of cholophæin in aqueous ammonia produce similar phenomena. If their colour is equal to that of a strong solution of potassium dichromate, the field of view appears perfectly black from the violet end to near the sodium line (50), and somewhat sharply defined. On diluting the solution, the colour gradually becomes yellow and green, but somewhat dull. Biliverdin in alcoholic solution exhibits absorption at both ends of the spectrum. In strongly coloured layers, it transmits only green light; in somewhat more dilute layers, first yellow, orange, and part of the red, afterwards blue and violet. Very dilute solutions absorb only the very extreme red (Maly, *Zeitschr. f. Chem.* [2] v. 365).

BILIFUSCIN.
BILIHUMIN. } See the preceding article.

BILINEURINE. See NEURINE.

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* Huppert remarks that similar colours are produced on covering nitric acid with other alcoholic extracts, and especially with alcohol alone (*Chem. Centr.* 1863, p. 864).

BILIPHÆIN, BILIPRASIN, BILIRUBIN, BILIVERDIN. See BILE-PIGMENTS.

BISMUTH. According to determinations by F. Field and J. Abel (*Chem. Soc. J.* xvi. 304), bismuth occurs in most sulphuretted copper ores, in about the same proportion as silver in galena.

The following process, devised by R. Vogel (*Dingl. pol. J.* clxvii. 187), is now adopted in Joachimsthal for extracting bismuth from ores not containing lead. The stamped ores are mixed with 58 p. c. wrought-iron turnings, and, according to their richness and composition, with 15 to 50 p. c. soda, 5 p. c. lime, and 5 p. c. fluor-spar, and fused in Hessian or plumbago crucibles. Arsenic and sulphur then separate, in combination with cobalt, nickel, and a small quantity of iron, in the form of speiss, and nearly the whole of the bismuth is obtained in the metallic state. A similar process (fusion with limestone and quicklime in proportion to the amount of silica, with addition of scraps of iron) is employed by Patera (*Jahresb.* 1862, p. 646) for the extraction of bismuth from refinery residues.

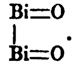
Estimation and Separation.—J. Löwe (*Jahresb.* 1859, p. 624) finds that basic bismuth nitrate, obtained by evaporating the nitric acid solution to a syrup, repeatedly mixing the residue with warm water, and evaporating over the water-bath, may be washed with a cold solution of ammonium nitrate (1 pt. in 500), without a trace of bismuth passing into the filtrate. He accordingly recommends this process for the quantitative estimation of bismuth and for separating this metal from lead, the nitrate of which is soluble in the dilute solution of ammonium nitrate. To separate bismuth from lead, copper, and cadmium together, the concentrated nitric acid solution is heated over the water-bath till the copper is wholly converted into insoluble basic nitrate, and the cooled residue is washed with ammonium nitrate, whereby lead and cadmium are dissolved, while the copper and bismuth remain behind, and may be dissolved in nitric acid, and separated by ammonium carbonate or potassium cyanide.

According to H. Rose (*Pogg. Ann.* cx. 411), bismuth may be very exactly estimated as *oxychloride*, BiClO, or $Bi^2Cl^3 . BiO^3$, which is quite insoluble in dilute hydrochloric acid. The solution, not containing too much free acid, is mixed with hydrochloric acid, and diluted with water, till no further turbidity is produced; and the precipitated oxychloride is washed with water on a weighed filter, and weighed, after drying at 100°. As however the precipitate is apt to lose a little chlorine by prolonged washing, it is better to reduce it by fusion with potassium cyanide, and weigh the metallic bismuth. This reduction is especially necessary when the solution contains sulphuric acid, as in that case the precipitate will contain a small quantity of basic bismuth sulphate. This mode of precipitation answers well for the separation of bismuth from copper, cadmium, cobalt, or zinc, but not from iron or lead.

Bismuth may also be very exactly estimated as *arsenate*, $2BiAsO^4 . H^2O$ (at 100°–120°), by precipitating the nitric acid solution with arsenic acid, disodic arsenate, or trisodic arsenate, washing the yellow precipitate with water by decantation, collecting it on a weighed filter, and weighing the precipitate and filter together, after drying at 120°. This method serves also for the separation of bismuth from cadmium. It cannot however be used for the estimation of arsenic acid, inasmuch as the bismuth arsenate is soluble in excess of acid bismuth-solutions (Salkowski, *Zeitschr. f. Chem.* [2] iv. 554).

According to Nicklès (*Bull. Soc. Chim.* [2] v. 49), bismuth may be distinguished from lead by means of *ammonio-thallic chloride* (v. 748), which gives a white precipitate with bismuth salts, but none with any salt of lead, excepting the basic acetate. The same reaction is exhibited by ammonio-thallic bromide.

Compounds of Bismuth.

Bismuth belongs to the nitrogen group of elements, being trivalent in its best defined compounds, quintivalent only in the pentoxide Bi^2O^5, and in the bismuthates $Bi^vO^2(OM)$; the so-called di-compounds of bismuth contain two atoms of trivalent bismuth in their molecule, the dichloride for example being $\begin{array}{l} Bi'''Cl^2 \\ | \\ Bi'''Cl^2 \end{array}$, the dioxide  $\begin{array}{l} Bi{=}O \\ | \\ Bi{=}O \end{array}$.

Tribromide. $BiBr^3$.—This compound may be prepared by adding pulverised bismuth to a mixture of equal parts of bromine and anhydrous ether. It is soluble in ether, and separates from the solution on evaporation in a vacuum, in deliquescent prisms which are decomposed by water (Nicklès, *Rép. Chim. pure*, i. 366). Its syrupy solution mixed with ammonium bromide yields yellow tables or prisms of a double salt: $2NH^4Br . BiBr^3 . 5H^2O$. The same compound is obtained in groups of transparent dichroic rhombic pyramids by heating an alcoholic solution of the two component bromides in a sealed tube.

Bismuth bromide heated with anhydrous ether to 100° in a sealed tube dissolves, forming two layers, the lower of which contains a compound of bismuth bromide and ether, crystallising on evaporation in very deliquescent rhombic prisms containing $BiBr^3 . C^4H^{10}O . 2aq.$: this compound destroys paper (Nicklès, *Rép. Chim. pure*, iii. 189).

Trichloride. $BiCl^3$.—A solution of this compound in hydrochloric acid leaves on evaporation, slender white needles of *hydrogen-bismuth chloride*, $BiCl^3 . 2HCl$ (Jacquelain, *Ann. Ch. Phys.* [2] lxii. 363).

Potassium-bismuth chloride, $BiCl^3 . 2KCl . \frac{5}{2}H^2O$, obtained by evaporating a solution of bismuth chloride in hydrochloric acid mixed with potassium chloride, crystallises, according to Rammelsberg (*Krystallogr. Chemie*, p. 213), in rhombic combinations, $\infty P . P . oP . \bar{P}\infty . \frac{1}{2}\breve{P}\infty$. Ratio of axes $a : b : c = 0{\cdot}6873 : 1 : 1{\cdot}7979$. Angle $\infty P : \infty P = 111°$; $P : P$ (brach.) $= 114° 36'$; $P : P$ (macr.) $= 76° 22'$; $P : P$ (basal) $= 145°$. The *sodium salt* $BiCl^3 . 2NaCl . 3H^2O$ is obtained in a similar manner. Both these salts are decomposed by water (Jacquelain).

When *ammonia gas* is passed over bismuth chloride contained in a retort, three different products are formed, one of which, being very volatile, passes into the receiver, while the other two remain in the retort. One of these, consisting of $2BiCl^3 . NH^3$, is red, fusible, and crystallisable; the other, $BiCl^3 . 2NH^3$, is dingy green, and difficult to purify: its composition was established by that of the double salt which it forms when treated with hydrochloric acid. The volatile compound is white, and consists of $BiCl^3 . 3NH^3$ (Déhérain, *Compt. rend.* liv. 724).

These ammoniochlorides treated with hydrochloric acid yield double chlorides of bismuth and ammonium, viz. $2BiCl^3 . NH^4Cl$, crystallising in deliquescent needles; $BiCl^3 . 2NH^4Cl$ in hexagonal laminæ, isomorphous with the corresponding antimony salt, and containing, according to Rammelsberg, $2\frac{1}{2}$ mol. water; and $BiCl^3 . 3NH^4Cl$ in rhombic laminæ (Déhérain). These double chlorides may also be obtained by evaporating acid solutions of bismuth chloride mixed in due proportion with sal-ammoniac. In preparing the last-mentioned compound by this method, the mother-liquors yield another salt, $2BiCl^3 . 5NH^4Cl$, in rhombohedral crystals with angles of 113° 32′ and 102° 22′ (Rammelsberg). Déhérain has also obtained a double chloride containing both potassium and ammonium, viz. $BiCl^3 . 2NH^4Cl . KCl$, which crystallises in rhombic laminæ.

A *seleniochloride*, containing $BiSeCl$ or $BiCl^3 . Bi^2Se^3$, is obtained by adding pulverised bismuth selenide to fused bismuth-ammonium chloride, heating the mass till it boils quietly, and no more unaltered bismuth selenide can be perceived in it, and treating the cooled mass with dilute hydrochloric acid. The seleniochloride then remains in small needle-shaped crystals having a dark steel-grey colour and metallic lustre. Heated in a stream of carbonic acid gas, it is resolved into chloride and selenide of bismuth, the former volatilising. It is also quickly and completely decomposed by strong nitric acid (R. Schreider, *Pogg. Ann.* xciv. 628).

Tri-iodide. BiI^3 (i. 594).—A solution of this compound in hydriodic acid yields by evaporation rhombic octohedrons of *hydrogen-bismuth iodide*, $BiI^3 . HI . 4aq.$ (Arppe).

Bismuth iodide forms a large number of double iodides, isomorphous with the corresponding compounds of antimony; they are obtained by direct union of the component iodides, or by the action of iodine on bismuth in presence of the iodide of another metal (Nicklès, *Compt. rend.* li. 1097; *Jahresb.* 1860, p. 176; *J. Pharm.* [3] xxxix. 116; *Jahresb.* 1861, p. 272. Linau, *Pogg. Ann.* cxi. 240; *Jahresb.* 1860, p. 177).

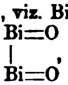
(1) $NH^4I . BiI^3 . H^2O$	Black needles; obtained by action of iodine on bismuth, in presence of ammonium iodide.
(2) $NH^4I . (Bi : Sb)I^3 . 2H^2O$	Black crystals yielding a red powder.
(3) $2NH^4I . BiI^3 . \frac{5}{2}H^2O$	Deposited from absolute alcohol in red crystals.
(4) $2NH^4I . BiBr^3 . \frac{5}{2}H^2O$	Dichroic deliquescent crystals; obtained by action of bromine on bismuth, in presence of ammonium iodide.
(5) $4NH^4I . BiI^3 . 3H^2O$	Dark red-brown rectangular prisms; powder cinnabar-red; obtained by direct combination.

(6) $KI.BiI^3.H^2O$	Black needles; prepared like (1).
(7) $NaI.BiI^3.H^2O$	Black-brown efflorescent crystals, yielding a red powder.
(8) $NaI.(Bi;Sb)I^3.2H^2O$	Obtained by treating a mixture of bismuth and antimony with iodine in presence of ammonium iodide.
(9) $3NaI.2BiI^3.12H^2O$	Garnet-red rectangular prisms; obtained by direct combination.
(10) $BaI^2.BiI^3.9H^2O$	Small, red, shining, rhombic prisms, black when dried at 250°.
(11) $CaI^2.BiI^3.9H^2O$	Dark red, shining, rhombic prisms, with basal end-face.
(12) $MgI^2.BiI^3.12H^2O$	Garnet-red rectangular prisms; anhydrous at 175°.
(13) $ZnI^2.BiI^3.12H^2O$	Resembles (12); anhydrous at 100°.

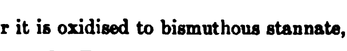
The last four double iodides are obtained by adding bismuth iodide to a concentrated solution of the other iodide and evaporating (Linau). Among the compounds examined by Nicklès, those containing $2H^2O$ crystallise in rhombic prisms of 97°; those with $1H^2O$ in right rhombic prisms of 135° 25′, with a dome and numerous secondary faces. All these double salts are more or less deliquescent, decomposible by water, and in some cases by alcohol, and cannot be recrystallised. They are quickly altered by light, especially by the violet rays, their surface acquiring a red colour—an alteration which likewise takes place in bismuth iodide itself (Nicklès).

Bismuth Sulphiodide, BiSI, may be obtained, as a sublimate composed of long needles, by disposing iodine, sulphur, and bismuth sulphide in alternate layers in a capacious crucible, and subjecting the whole to a prolonged calcination (Linau).

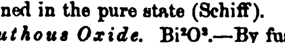
Oxides. Bismuth forms four oxides, viz. Bi^2O^2, Bi^2O^3, Bi^2O^4, and Bi^2O^5.

The *dioxide* or *suboxide*, Bi^2O^2 or  $\begin{matrix}Bi{=}O\\ | \\ Bi{=}O\end{matrix}$, is formed by the action of the air on bismuth heated a few degrees above its melting point; also by reduction of bismuth salts, with stannous chloride for example. To prepare it, bismuth trioxide and stannous chloride in equivalent proportions are dissolved in hydrochloric acid; the mixed solution is poured into moderately strong aqueous potash; and the resulting black-brown precipitate of stannic oxide and bismuth dioxide is treated with strong potash-ley, which dissolves the stannic oxide and leaves the bismuth dioxide. The latter dried at 100° is a greyish-black crystalline powder, very difficult to reduce, but easily oxidisable, burning in the air like tinder (Schneider, *Pogg. Ann.* lxxxviii. 45; Schiff, *Ann. Ch. Pharm.* cxix. 331).

Bismuth dioxide shows but little tendency to unite with acids, but it exists in the form of stannate in the precipitate obtained in preparing it. This stannate is also produced, as a compound of a deep yellow colour, when a solution of stannous chloride is poured upon pulverised bismuth nitrate; if the operation is performed at ordinary temperatures, the compound may be preserved unaltered for several days; but on applying heat, it changes to a brown or grey-black powder, which, however, when washed with water, is reconverted into the yellow compound. The latter dried at 100° is of a deep orange or ochre-yellow colour, insoluble in water and in dilute acetic acid, but soluble in mineral acids, the solutions giving a black precipitate with potash. The yellow compound consists of

$SnBi^4O^6$ or  or $(\overset{iv}{Bi^2}O^2)^2\left\{\begin{matrix}Sn^{iv}\\O^2\end{matrix}\right.$.

By heating in the air it is oxidised to bismuthous stannate,

$SnBi^4O^8$ or  or $Sn^{iv}(BiO^2)^4$.

Potash removes the stannic oxide from the salt $SnBi^4O^6$, leaving the bismuth dioxide, which may thus be obtained in the pure state (Schiff).

Trioxide or Bismuthous Oxide. Bi^2O^3.—By fusing the ordinary pulverulent oxide with potassium hydrate, it may be obtained in rhombic prisms, $\infty P . oP . \frac{4}{3}\breve{P}\infty . \frac{3}{2}\breve{P}\infty$. Axes $a : b : c = 0{\cdot}8165 : 1 : 1{\cdot}0640$ (Nordenskjöld, *Pogg. Ann.* cxiv. 512).

Pentoxide. Bismuthic Oxide or Anhydride. Bi^2O^5.—Formed by heating the corresponding hydrate to 130°; also, according to Schönbein (*Jahresb.* 1864, p. 174), by the action of ozone on metallic bismuth. It is easily reducible, giving off part of its oxygen when heated a little above 130°; being instantly decomposed by hydrochloric acid; with evolution of chlorine and formation of bismuth trichloride, and by strong sulphuric or nitric acid, with evolution of oxygen; dilute nitric acid does not act upon it; according to Arppe, boiling nitric acid converts it into an oxide containing Bi^4O^9. It is not attacked by aqueous alkalis. According to Schönbein, it decomposes hydrogen dioxide, and is itself reduced to Bi^2O^4.

Bismuthic Hydrate, Hydrogen Bismuthate, or *Bismuthic Acid,* $HBiO^3$ or $H^2O.Bi^2O^5$, analogous in composition to nitric acid, HNO^3, is produced by the action of chlorine on bismuthous hydrate suspended in concentrated potash-ley (i. 594). Another bismuthic hydrate, $2Bi^2H^4O^7$ or $Bi^2O^5.2H^2O$ (corresponding to pyrophosphoric acid), is obtained by treating a solution of bismuth nitrate with excess of potassium cyanide. It is a dark brown powder which gives off its water at 150°, and is reduced to trioxide by subsequent ignition in a glass tube (Bödeker, *Ann. Ch. Pharm.* cxxiii. 61).

The *tetroxide,* or *Bismuthous Bismuthate,* $Bi^2O^4 = \left.\begin{matrix}Bi^{v}\\Bi'''\end{matrix}\right\}O^4 = \left.\begin{matrix}(Bi^{v}O)'''\\Bi'''\end{matrix}\right\}O^4 = Bi^2O^3.Bi^2O^5$, is produced when the trioxide is treated with oxidising agents in presence of an alkali. When chlorine is passed into cold aqueous potash of sp. gr. 1·385 containing bismuth trioxide in suspension, a yellow, red, or brown oxide is formed, which when heated with strong nitric acid, is converted into an orange-yellow hydrate, $Bi^2O^4.2H^2O$, which gives off its water at 150°, leaving the light brown tetroxide (Schrader, *Ann. Ch. Pharm.* cxxi. 204; *Jahresb.* 1861, p. 269). With still more concentrated potash-ley, bismuthic acid is produced (*vid. sup.*). The tetroxide may also be prepared by adding basic bismuth nitrate, gradually and with constant stirring, to sodium hydrate fused at a low red heat in an iron dish, continuing the heating and stirring till the mass has become black-brown, or nearly black, boiling the decanted and pulverised mass with water, digesting the undissolved reddish-brown powder with cold dilute nitric acid, then washing and drying it (Böttger, *J. pr. Chem.* lxxiii. 494).

Selenide. Bi^2Se^3.—According to R. Schneider (*Pogg. Ann.* xciv. 628), the selenide prepared, according to the method of Berzelius, by fusing bismuth with selenium (i. 595), generally contains excess of bismuth. The pure selenide obtained by fusing 2 at. bismuth with 3 at. selenium, and frequently remelting the product with fresh addition of selenium out of contact with the air, exhibits on the newly fractured surface a light steel-grey colour, metallic lustre, and distinct crystallo-granular structure; it has a sp. gr. of 6·82, the hardness of galena, and is easily pulverised. It is scarcely attacked by strong hydrochloric acid, even at the boiling heat, but easily and completely decomposed by nitric or nitromuriatic acid. With bismuth chloride it forms the compound BiClSe or $BiCl^3.Bi^2Se^3$ (p. 347).

Sulphide. Bi^2S^3.—A compound of this sulphide with *potassium sulphide,* $K^2Bi^2S^4 = K^2S.Bi^2S^3$, is obtained in light steel-grey shining needles, by fusing 1 pt. pulverised bismuth, 6 pts. dry potassium carbonate, and 6 pts. sulphur, and exhausting the fused mass with water, in which the double sulphide is soluble (R. Schneider, *Zeitschr. f. Chem.* [2] v. 630).

An *oxysulphide* of bismuth, Bi^4SO^3, occurs native as *Karelinite* in the Altai (iii. 445). An artificial oxysulphide may be prepared by heating the trioxide with sulphur to low redness in a retort. The mass blackens, gives off sulphuric oxide, and then the excess of sulphur, leaving a grey scoriaceous mass having a faint metallic lustre, becoming strong by burnishing, and a sp. gr. of 6·31. It contains no metallic bismuth, but if again strongly ignited, gives off sulphurous oxide and then exhibits small globules of bismuth. A product obtained in this manner by igniting 142 pts. bismuth trioxide with 40 parts of sulphur, yielded by analysis numbers which may be represented by the formula $Bi^6S^4O^3$, or perhaps $Bi^2O^3.2Bi^2S^2$ (R. Hermann, *J. pr. Chem.* lxxv. 452).

BITUMENE. This name is given by Berthelot to the least volatile of the hydrocarbons obtained by passing benzene vapour through a porcelain tube heated to bright redness. On distilling the liquid portion of the product the bitumene remains in the retort, even at a red heat, as a blackish liquid, which solidifies on cooling. It dissolves only in boiling ether, and in small quantity, forming a fluorescent liquid, which leaves a metallically lustrous film on evaporation (*Bull. Soc. Chim.* [2] vi. 272).

BIURET. $C^2H^5N^3O^2 = \left.\begin{matrix}CO''\\CO''\end{matrix}\right\}\left\{\begin{matrix}NH^2\\NH''\\NH^2\end{matrix}\right.$.—This compound is formed, together with monocyanurate of urea, on passing the vapour of cyanic acid into melted urea, till a solid mass is produced. It is isomeric with cyanate of urea, and probably stands to the latter in the same relation as urea to cyanate of ammonium (Finck, *Ann. Ch. Pharm.* cxxiv. 331). It is also produced, together with phenate of ammonium, on dissolving urea in phenol at 150°–160°, and may be extracted from the solid mass which forms on cooling, by washing with ether, boiling the aqueous solution of the residue with hydrated lead oxide, and evaporating the solution after freeing it from lead. It appears from this reaction that urea when heated with phenol decomposes in the same manner as when heated alone, namely into biuret and ammonia (i. 600): $2CH^4N^2O = C^2H^5N^3O^2 + NH^3$ (Baeyer, *Ann. Ch. Pharm.* cxxxi. 251).

According to Huppert a. Dogiel (*Zeitschr. f. Chem.* [2] iii. 691), the easiest way of preparing biuret from urea is to treat the urea with chlorine at 150° till the mass becomes pasty. The product, consisting chiefly of biuret, is freed from cyanuric acid, formed at the same time, by precipitation with basic lead acetate.

Biuret is also produced by the action of ammonia on allophanic ether; in fact, it has the composition of allophanic amide, $N\left\{\begin{matrix}C^2H^3N^2O^2\\H^2\end{matrix}\right.$ (Huppert a. Dogiel).

The aqueous solution of biuret mixed with *silver sulphate* yields, on addition of ammonia, a precipitate of silver cyanurate, and the filtrate freed from silver and evaporated yields crystals of urea and urea nitrate. Biuret dried at 120° slowly absorbs *hydrochloric acid* gas at 100°, forming the hydrochloride $2C^2H^5N^3O^2.HCl$, which, when heated to 160°–170° in the stream of hydrochloric acid gas, gives off water and carbon dioxide, leaving a yellowish white tumid mass, partially soluble in cold, completely in hot water. The portion easily soluble in cold water contains sal-ammoniac, together with hydrochloride of guanidine, while the less soluble portion consists of cyanuric acid and monocyanurate of urea:

$$\underset{\text{Biuret.}}{2C^2H^5N^3O^2} = NH^3 + \underset{\text{Urea cyanurate.}}{CH^4N^2O.C^3H^3N^3O^3}$$

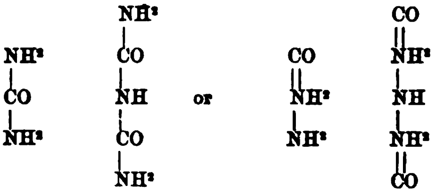
$$\underset{\text{Biuret.}}{C^2H^5N^3O^2} = CO^2 + \underset{\text{Guanidine.}}{C^2H^5N^3}$$

Biuret boiled with strong hydrochloric acid yields sal-ammoniac, together with small quantities of urea and guanidine hydrochloride. With *nitric acid*, it forms cyanuric acid, urea nitrate, and, as ultimate product, ammonium nitrate. By boiling with *baryta-water*, it is decomposed in the manner represented by the equation:

$$\underset{\text{Biuret.}}{C^2H^5N^3O^2} + H^2O = \underset{\text{Urea.}}{CH^4N^2O} + NH^3 + CO^2.$$

(Finck, *loc. cit.*)

The relation of biuret to urea may be represented by the following formulæ:



Urea. Biuret. Urea. Biuret.

BIXIN, the red resinous colouring matter of annotto (the red paste obtained by crushing the seeds of *Bixa Orellana*), has been examined by Bolley a. Mylius (*Bull. Soc. Chim.* [2] iii. 330), who assign to it the empirical formula $C^5H^6O^2$, and by W. Stein (*J. pr. Chem.* cii. 175), according to whose analyses it has the composition $C^{15}H^{18}O^4$.

Bolley a. Mylius prepare it by digesting the dried alcoholic extract of annotto with ether; repeatedly treating the least soluble portion (which contains the greater part of the colouring matter) with hot ether; dissolving the remainder in alcohol; precipitating the alcoholic solution with lead acetate; decomposing the washed precipitate with hydrogen sulphide; extracting the colouring matter therefrom by hot alcohol; and precipitating the alcoholic solution with water. Stein examined bixin prepared by De Vrij from the fresh fruits of *Bixa Orellana* by treating them with alkaline water, precipitating the solution with sulphuric acid, and repeatedly boiling the precipitate with water and ether to remove a bitter principle and resin.

Pure bixin is an amorphous substance of the colour of vermillion, not melting at 145°, nearly insoluble in water, slightly soluble in cold alcohol and in ether, easily soluble in hot alcohol and in alkalis. It is not altered by dilute sulphuric or hydrochloric acid; dilute nitric acid turns it yellow; strong nitric acid converts it into a yellow substance precipitable by water and smelling like musk (Bolley a. Mylius). According to Stein, it dissolves in 25·4 pts. boiling and 89 pts. cold alcohol, in 345 pts. ether, 3435 pts. carbon bisulphide, 93·3 pts. chloroform; also in alkalis and alkaline carbonates. The bitter, yellow, or brown-red alcoholic solution gives an orange precipitate with neutral lead acetate; brown-yellow with mercuric chloride and cupric acetate; brown-red with ferric chloride; reddish-yellow with aluminium acetate; and deep yellow with stannous or stannic chloride on addition of ammonia. When boiled with hydrochloric acid it deposits a brown substance. Aqueous sulphurous acid partially decolorises the solution at the boiling heat. Bixin fused with potassium hydrate forms a black-brown amorphous product. It is coloured deep blue by strong sulphuric acid, and forms nitro-compounds when treated with fuming nitric acid.

When a solution of bixin in very weak spirit is saturated with chlorine, chlorobixin, $C^{15}H^{16}Cl^2O^5$, separates as a white cloud, forming when dry a yellow-brown amorphous powder, insoluble in water, easily soluble in alcohol and ether. The action of chlorine also gives rise to other products richer in chlorine and less soluble in ether.

Nascent hydrogen converts bixin, in acid or alkaline solution, into a substance insoluble in water, and drying up to a brownish amorphous mass whose percentage composition is expressed by the formula $C^{28}H^{38}O^7$ (Stein).

BLOOD. The following are recent determinations of various constituents of the blood:

Iron.—According to Pelouze (*Compt. rend.* lx. 880), the blood of various warm-blooded animals contains in 10,000 pts. by weight, the following quantities of iron:

	Man	Ox	Pig	Goose	Turkey	Domestic Fowl	Duck	Frog
Max.	537	540	595	358	336	357	344	425
Min.	506	480	506	347	333	—	342	

Hæmoglobin.—See p. 352.

Cholesterin, Protagon, and *Fats.*—Hoppe-Seyler (*Medicin.-chem. Unters.* i. 140; *Jahresb.* 1866, p. 745) has determined the quantity of cholesterin in goose- and ox-blood: I. and II., from very fat young geese; III. and IV., from a fat old goose; V. from the ox:

In the Blood-corpuscles.

	I.	II.	III.	IV.	V.
Grm. cholesterin in 100 c.c. blood.	0·043	0·052	0·040	0·060	0·048.

In the Serum.

	I.	II.	III.	IV.
Grm. cholesterin in 100 c.c. blood.	0·234	0·314	0·019	0·035.

The amount of cholesterin in the corpuscles (0·04–0·06 grm. in 100 c.c. blood) is independent of the amount of cholesterin and of fat in the serum or plasma. The proportion of the same substance in the serum varies considerably, increasing and diminishing with the amount of fat. The corpuscles of the same kinds of blood were found to contain no saponifiable fats, even when the serum was very rich in fat. The serum may contain a large quantity of saponifiable fats, together with cholesterin and protagon.

Sugar and *Alcohol.*—Respecting the presence of sugar in blood, see GLYCOGEN (ii. 907). According to T. H. Ford (*Jahresb.* 1861, p. 792), blood in its normal state contains a minute quantity of alcohol produced by fermentation of the sugar.

Urea.—Poisseuille a. Gobley (*Compt. rend.* xlix. 164) found in 1,000 grammes of the blood of herbivorous and carnivorous animals, an average quantity of 0·220 grm. urea. Hence, supposing that the kidneys of an adult man are traversed by 1,000 kilogrammes of blood in 24 hours, and that out of the 220 grms. of urea therein contained, 20 grms. are separated in the urine, they conclude that 200 grms. are returned into the circulation.

Trimethylamine.—According to Dessaignes (*J. Pharm.* [3] xxxii. 43; *Jahresb.* 1857,

p. 382), calf's blood, twelve hours after removal from the vessels, contains a small quantity of trimethylamine, emitting the peculiar crab-like odour of that base when agitated with milk of lime. The fresh blood does not exhibit this odour.

Hæmoglobin, Hæmatoglobin, or **Hæmatocrystallin** (Hoppe-Seyler, *Med.-chem. Unters.* i. 169; *Zeitschr. f. Chem.* [2] v. 243; *Jahresb.* 1867, p. 798).—This substance is the only colouring matter of the blood of vertebrate animals. The red corpuscles of the blood of man and many other mammalia consist almost exclusively of hæmoglobin, but in those of certain mammalia and birds the hæmoglobin is associated with considerable quantities of albuminous substances.

Preparation.—The separation of the corpuscles from the plasma or serum is best effected by mixing the blood—after separating the fibrin by beating it for ten minutes with a stick or a goose feather, and filtering through a linen cloth—with 1 vol. of a saturated solution of common salt and 9 vol. distilled water, and repeatedly washing the precipitated magma with the same liquid. To separate the hæmoglobin from the other constituents of the corpuscles (proteids, cholesterin, a substance rich in phosphorus, which swells up in water, potassium chloride, and sodium phosphate), the washed magma is agitated with a small quantity of water and from 4 to 10 times its volume of ether; the ether is drawn off after some hours; the removal of the cholesterin is completed by repeated agitation with ether; and the red watery liquid is filtered. The solid matter collected on the filter consists of coagulated proteids, mixed, in the case of dogs', guinea-pigs', or squirrels' blood, with crystals of hæmoglobin. The ethereal solution contains the whole of the cholesterin, together with part of the phosphorised substance; and the aqueous solution contains the remainder of the latter, together with hæmoglobin, alkali-salts, and a (still unknown) nitrogenous extractive matter.

Crystallised Hæmoglobin (*Oxyhæmoglobin*).—The aqueous solution obtained as above from the blood of the dog, guinea-pig, rat, or squirrel is for the most part immediately converted at low temperatures into a pulp of hæmoglobin crystals. The same crystals may be obtained from the blood of birds by cooling the clear deep red aqueous solution to 0°, mixing it, while stirring, with ¼ vol. of 80 p. c. alcohol also cooled to 0°, and leaving the mixture to itself for a few days at a temperature of −5° to −10°. To purify the crystals, they are washed on a filter with a cooled mixture of 1 vol. alcohol and 4 vols. water, pressed in the filter, stirred up with from 5 to 30 times their volume of water, according to their solubility; and the liquid, after being heated to 30° or 40°, is quickly filtered. It is then cooled to 0°, shaken up with air, mixed with ¼ vol. alcohol, and left to crystallise. After several repetitions of this treatment (which may likewise be applied to the crystals which separate from the blood of the dog and other animals on addition of ether), the hæmoglobin is obtained pure, in the form of a vermillion-coloured pasty mass, which when dried below 0° yields a light brick-red powder. From many kinds of blood, especially that of man, and of the ox, sheep, and pig, it cannot be obtained by this process in any considerable quantity (forming at most an amorphous precipitate), and the preparation succeeds for the most part only at low temperatures. Above 0° the solutions quickly assume a dark colour from decomposition, and are then difficult to crystallise. If the solution cooled below 0° be gradually mixed with alcohol cooled to a very low temperature, amorphous hæmoglobin separates, which is soluble in water, but is reprecipitated by alcohol in the amorphous state. All other modes of preparation were found by Hoppe-Seyler to yield less satisfactory results. The crystals are mostly prismatic, but those of the rat and mouse are tetrahedral, those of the squirrel six-sided tables. They are sparingly soluble in cold water, more soluble in warm water, and freely soluble in feebly alkaline solutions, such as serum.

Amorphous hæmoglobin may be obtained, not quite pure, from any of the kinds of blood above mentioned in the following manner. The defibrinated blood—or better the isolated blood-corpuscles—is agitated with water and ether; the aqueous solution, after separation from the ether, is precipitated with basic lead acetate; the liquid quickly filtered; and the lead separated from the filtrate by potassium carbonate. To the ice-cold solution, pulverised potassium carbonate is added till the colouring matter is completely precipitated; and the precipitate is washed at 0° with a nearly saturated solution of the same salt, and pressed between paper. It may be freed from the greater part of the potassium carbonate by diffusion in water, but is apt to undergo partial decomposition at the same time. Amorphous hæmoglobin may be separated in the same manner from the solution of the hæmoglobin crystals. If the solution is mixed with several volumes of alcohol (instead of potassium carbonate), part of the hæmoglobin becomes insoluble in water, and is subsequently decomposed.

Hæmoglobin from the blood of the dog and of the goose, repeatedly crystallised and dried at 110°–120°, exhibited the following composition:

	C	H	N	S	Fe	O	P^2O^5		
Dog	53·85	7·32	16·17	0·39	0·43	21·84	—	=	100
Goose	54·26	7·10	16·21	0·54	0·43	20·69	0·77	=	100.

The crystals, after drying in a vacuum at 0°, experience at 110°–120° a loss of weight due chiefly to water, but partly also to loosely combined oxygen, and amounting in the crystals from dogs' blood to 3·4 p. c., in those from goose-blood to 7·2 p. c.

In contact with alkalis or acids, hæmoglobin is resolved into hæmatin and globulin. Treated with a great excess of glacial acetic acid, in presence of metallic chlorides, it yields globulin and hæmatin hydrochloride (hæmin) amounting to 3·86 p. c. of the hæmoglobin.

The optical properties (absorption-spectrum) of hæmoglobin, and its functions as a carrier of oxygen, are described under RESPIRATION (v. 89). The method of spectral analysis has been applied by W. Preyer (*Ann. Ch. Pharm.* cxl. 187) to the determination of the quantity of hæmoglobin in blood. The determination depends upon the fact that a concentrated solution of hæmoglobin in a layer of a certain thickness is opaque, even in strong illumination, to all rays excepting the red, whereas less concentrated solutions in a layer of the same thickness give passage to other rays besides the red and orange, and especially to a portion of the green. If, therefore, a measured quantity of blood placed before the slit of the spectral apparatus be diluted with water till green light appears in the spectrum, then, if the proportion of hæmoglobin in a solution which transmits the green under exactly similar circumstances has once for all been determined, it is easy to estimate the percentage of hæmoglobin in the blood under examination. Preyer's determinations made in this manner agree very nearly with the quantities of hæmoglobin calculated from the amount of iron in the same samples (0·42 p. c. of the hæmoglobin). The mean quantities of hæmoglobin in blood from various animals were as follows (A estimated by the amount of iron; B by the spectral method):

	Dog	Sheep	Ox	Pig	Cock	Duck
A	13·8	11·2	11·4–13·0	12·0–14·1	8·51–2·7	8·1
B	13·3	11·2	13·6	14·3	9·0–9·8	9·3

These results further show that hæmoglobin is the only ferruginous constituent of the blood-corpuscles.

Solutions of hæmoglobin free from oxygen are not perceptibly altered by *hydrogen sulphide*, or at least only after several days, even in presence of ammonia. But on treating oxyhæmoglobin with the same reagent, several alterations take place simultaneously or successively. The first action (which shows itself also in the ammoniacal solution) is the separation of the loosely combined oxygen from the hæmoglobin, which is accelerated by heat, but always requires some time. In the ammoniacal solution of the colouring matter this abstraction of oxygen is the only reaction that takes place; but in the neutral solution another change soon shows itself by the appearance of an absorption-band at the red of the spectrum (from 67 to 72 of the scale on which C stands at 61 and D at 80). The colouring matter characterised by this band is distinguished from hæmatin and from meta-hæmoglobin (*q.v.*) by the fact that the solutions of these two substances, when treated with ammonia and ammonium sulphide exhibit the bands in the green from 86 to 94 and 102 to 110, whereas the band of the colouring matter produced from oxyhæmoglobin in the way just described remains unaltered when thus treated. From its mode of formation, Hoppe-Seyler regards it as a sulphur-compound of hæmatin or hæmoglobin. By the further action of hydrogen sulphide, this compound is decomposed (with separation of sulphur and an albuminous substance), whilst a body is formed which is olive-green in thin, brown-red in thicker layers, and dries up to a brittle hygroscopic mass having a pitchy lustre. This substance in aqueous solution is coagulated by heating, also by alcohol and acids. It contains all the iron (0·44 p. c.) of the hæmoglobin, and about four times as much sulphur (1·57 p. c. instead of 0·415). A solution of iron sulphide (as obtained with very dilute ferrous sulphate, tartaric acid, and ammonium sulphide) exhibits an absorption-band in the red, like that of the solution of hæmoglobin treated with oxygen and with hydrogen sulphide. But no formation of iron sulphide can take place in the above-described reaction, on account of the presence of oxygen; moreover, the product, as above stated, contains all the iron of the hæmoglobin.

According to Nawrocki (*Zeitschr. anal. Chem.* vi. 285; *Jahresb.* 1867, p. 802), ammonium sulphide exerts on hæmoglobin at first merely a reducing, but afterwards a rapid decomposing action. A solution of hæmoglobin mixed with $\frac{1}{2}$ vol. of ordinary ammonium sulphide exhibits a dark band in the red at the line C; the broad reduction-band (between D and E) becomes narrower and more sharply defined: and afterwards a second broader band appears, covering E and extending beyond *b*. After the appearance of these bands, which disappear in about 24 hours, those of oxyhæmoglobin are no longer reproduced by agitation with air. According to W. Preyer (*Jahresb.* 1867, p. 802), *potassium persulphide* also causes the two bands of oxyhæmoglobin solutions to disappear, and at first brings out the band of reduced hæmoglobin, but afterwards, especially on gentle heating, a sharply defined black band, beginning at $\frac{7}{20}$ of the distance from D to E and ending at $\frac{12}{20}$ of the same distance, and a further band beginning at $\frac{17}{20}$ of the distance from D to E and ending at $\frac{5}{8}$ of that from E to *b*, make their appearance. At the boiling heat these bands disappear, the spectrum becoming shady, but reappear if the solution be quickly cooled. Solutions of the compound of hæmoglobin with carbon monoxide are altered by potassium sulphide only at the boiling heat, and again exhibit the two bands above mentioned on cooling. According to Hoppe-Seyler (*Medicin.-chem. Unters.* i. 299), the action of potassium sulphide and ammonium sulphide on oxyhæmoglobin takes place only in presence of free alkali, and depends on the formation and reduction of hæmatin.

Compound of Hæmoglobin with Carbon Monoxide.—By passing a stream of the gas, with frequent agitation, through an aqueous solution of blood-crystals, blood-corpuscles, or even defibrinated blood, cooling the liquid to 0°, mixing it with $\frac{1}{4}$ vol. cold alcohol, and leaving it to itself at or below 0°, bluish-red crystals are obtained less soluble and less easily decomposible than those of oxyhæmoglobin, with which they agree in external form. The solution, which is also bluish-red, gradually gives up its carbon monoxide when heated in a vacuum (100 grms. of the dry compound yielded 10·22 c.c. carbon monoxide) (Hoppe-Seyler).

Blood which has been treated with carbon monoxide exhibits, when properly diluted, almost exactly the same absorption-bands in the spectrum as oxygenated blood (v. 87); but these bands do not disappear on addition of ammonium sulphide even after several days, whereas when oxygenated blood free from carbon monoxide is mixed with ammonium sulphide, it exhibits after a few minutes only a single absorption-band midway between D and E. By this unalterability of blood containing carbon monoxide by ammonium sulphide, the presence of carbon monoxide may be detected in the blood of animals which have been poisoned even with small quantities of it (Hoppe-Seyler, *Zeitschr. anal. Chem.* iii. 439; *Jahresb.* 1865, p. 745). See also Pokrowsky and W. Kühne (*ibid.*). Potassium sulphide acts upon the compound of hæmoglobin with carbon monoxide only at the boiling heat, the liquid on cooling again exhibiting the two characteristic absorption-bands (Preyer, *Jahresb.* 1867, p. 802). Nawrocki (*ibid.* xvi. 640) finds that the quantity of oxygen displaced from arterial blood by passing a stream of carbon monoxide through it is equal to that which is evolved from the blood on placing it in a very perfect vacuum.

Compound of Hæmoglobin with Nitrogen Dioxide.—On passing nitrogen dioxide into a solution of the preceding compound, protected as far as possible from access of air, the carbon monoxide is displaced, and a compound of hæmoglobin with nitrogen dioxide is formed. The oxygen of oxyhæmoglobin is likewise displaced by nitrogen dioxide. The quantity of the gas absorbed by arterial blood is, however, but small. Blood from the crural artery of a dog took up, after addition of baryta-water, from 25·4 to 27·6 vol. p. c.; defibrinated dogs' blood 23 vol. p. c.; defibrinated ox-blood 31·8 vol. p. c. (reduced to 0° and 1 metre pressure). Blood saturated with nitrogen dioxide exhibits the same two absorption-bands as oxygenated blood; but the entire spectrum is darkened at the same time, and the progress of illumination on diluting the solution is different from that which takes place with oxyhæmoglobin.

Compounds of Hæmoglobin with Hydrogen Cyanide and Potassium Cyanide.—A concentrated solution of guinea-pigs' or dogs' blood mixed with prussic acid, deposits, on addition of $\frac{1}{4}$ vol. alcohol and cooling to 0°, crystals which are undistinguishable in appearance from those of oxyhæmoglobin, but still retain hydrogen cyanide even after repeated crystallisation and drying in a vacuum; the hydrogen cyanide may, however, be separated by distillation with water and a few drops of dilute sulphuric acid. This compound is more stable than pure oxyhæmoglobin, its solution not becoming perceptibly darker at temperatures above 0°.

The absorption-spectrum of blood is not altered by addition of prussic acid. A solution of blood or of oxyhæmoglobin enclosed in a tube, together with a few drops of prussic acid and a very small quantity of air, and left for several months, still exhibits the two absorption-bands of oxyhæmoglobin, whereas if no prussic acid be added, nothing but the bands of reduced hæmoglobin can be seen, even after a few days. *Mercuric cyanide* exerts the same conservative action as hydrogen cyanide on hæmoglobin, whereas all other mercury salts and all acids decompose it. The blood-corpuscles themselves do not appear to take up hydrogen cyanide (Hoppe-Seyler).

Solutions of *potassium cyanide*, either concentrated or dilute, do not affect the optical characters of hæmoglobin at ordinary temperatures; but on raising the mixture to the temperature of the animal body, the two characteristic absorption-bands disappear, and a broad band comes to light somewhat nearer to the violet than that of reduced hæmoglobin. In this solution—which has a yellowish tint, is very permanent, and does not coagulate when heated—the two absorption-bands of oxyhæmoglobin are not reproduced by the action of a stream of oxygen. On adding ammonium sulphide, the broad band disappears, and a new spectrum is formed with two bands from $\frac{5}{20}$ to $\frac{10}{20}$ of the distance from D to E, and from $\frac{13}{20}$ between D and E as far as $\frac{3}{4}$ from E to *b*. This spectrum is very much like that of the compound of hæmoglobin with carbon monoxide (the bands of the latter extend from $\frac{5}{40}$ to $\frac{17}{40}$ between D and E, and from $\frac{27}{40}$ between D and E as far as $\frac{7}{8}$ from E to *b*). If the solution be subjected to the action of oxygen, the broad band reappears, and on repeated addition of ammonium sulphide the two other bands are reproduced; the solution is then also coagulated by heat. Hydrogen cyanide and ammonium sulphide, with aid of heat, produce the same phenomena, viz. disappearance of the bands of oxyhæmoglobin, appearance of the broad band, and then of the two bands; the reaction is moreover attended with separation of sulphur. On passing oxygen into the liquid, these appearances are reversed as far as the transient appearance of the oxyhæmoglobin bands. Hence it appears that the compounds of hydrogen cyanide and potassium cyanide with hæmoglobin also contain oxygen, which is removed by ammonium sulphide, but is more intimately combined than in oxyhæmoglobin, and that in presence of hydrogen cyanide or potassium cyanide, hæmoglobin cannot be converted into oxyhæmoglobin.

When potassium cyanide is added to the aqueous solution of the compound of hæmoglobin with carbon monoxide, the characteristic absorption-bands do not disappear till the mixture is heated to 40°, whereupon the above-mentioned broad band appears, and on addition of ammonium sulphide is further altered in the manner already described; by agitation with air, the broad band is reproduced, and afterwards the orignal spectrum of the carbonic oxide compound. Hydrogen cyanide and ammonium cyanide act in the same manner with aid of heat; but the filtered solution, after agitation with air, finally exhibits the bands of oxyhæmoglobin (Preyer, *Zeitschr. anal. Chem.* vi. 289; *Jahresb.* 1867, p. 803). According to Nawrocki (*Jahresb.* 1867, p. 204), the broad absorption-band produced in a solution of hæmoglobin on heating with potassium cyanide, belongs, not to hæmoglobin, but to hæmatin. It is obtained immediately and without heating if the solution of hæmoglobin, before the addition of potassium cyanide, be mixed with caustic potash.

Hæmatin. $C^{96}H^{102}N^{12}Fe^{2}O^{18}$.—This substance was formerly regarded as the red colouring matter of the blood. The investigations of Hoppe-Seyler have shown, however, that it does not exist ready-formed in blood, but is produced, together with globulin, from hæmoglobin when blood is treated with acids or alkalis (p. 353). It may be obtained pure by dissolving its hydrochloride (hæmin) in ammonia, evaporating to dryness, heating the residue to 130°, dissolving out the ammonium chloride by water, and heating the residue to 130° (Hoppe-Seyler); also by mixing defibrinated blood (or blood agitated with ether as long as it will take up that liquid, and filtered) with a strong solution of potassium carbonate, till the liquid adhering to the separated coagulum becomes colourless; drying the coagulum on a filter at a temperature not above 50°; and digesting it for some days with absolute alcohol in a close vessel at a moderate heat (below 50°). The red liquid filtered therefrom is an alcoholic solution of hæmatin (Wittich, *J. pr. Chem.* lxi. 11).

In acid liquids, as in the hot extract of blood with acidulated alcohol, the spectrum of hæmatin exhibits a very faint absorption of the light from the middle space between the lines A and *a* to the middle between *b* and C. On diluting with alcohol, a sharply defined absorption-band appears between C and D, near C; and on further dilution, two absorption-bands appear in the green, faintly defined and soon vanishing (Hoppe-Seyler, *Jahresb.* 1865, p. 667). According to Nawrocki (*Zeitschr. anal. Chem.* vi. 285; *Jahresb.* 1867, p. 804), the spectrum of hæmatin is best seen in the ethereal solution obtained by mixing diluted blood with a little acetic acid and an equal volume of ether. This solution exhibits a band coinciding with C, a second before E, and a third fainter one between *b* and F. The brown solution of hæmatin in potash or potassium cyanide exhibits least absorption of light near the line C; on diluting this solution there remains a band between D and E, but nearer to D, which, however, likewise disappears while the solution still exhibits a strong colour: hydrochloric acid throws down from it unaltered hæmatin. Hence it appears that hæmatin forms with potassium cyanide a double cyanogen-compound, which, like the double metallic cyanides, differs in colour from the other compounds of hæmatin with acids or bases (Hoppe-Seyler, *loc. cit.*). According to Nawrocki, alkaline solutions of hæmatin (hæmin-crystals or Wittich's hæmatin) dissolved in ammonia give a spectrum with a band between C and D; but after treatment with a ferrous salt or with stannous chloride, they exhibit two other bands, which do not disappear on agitation with air, and are likewise visible for some time in the red ethereal solution obtained by mixing the ammoniacal liquid with ether and glacial acetic acid; but in this they gradually merge into the three bands of the normal hæmatin solution. If, on the other hand, the alkaline solution of hæmatin be mixed with ammonium sulphide, the liquid exhibits the same bands as hæmoglobin when similarly treated, and no longer yields up anything to ether on addition of acetic acid. Even very dilute solutions of putrefied blood exhibit this reaction with ammonium sulphide very distinctly (Nawrocki). Hæmatin (or hæmin) heated for some time with ammonia or a fixed alkali is converted into a body, the solution of which in acidulated alcohol or in an alkali has a dingy olive-green colour, dark red in thicker layers, and after treatment with reducing agents does not exhibit the spectrum of reduced hæmatin; neither can hæmin crystals be obtained from it (Hoppe-Seyler, *Jahresb.* 1867, p. 806).

By dissolving hæmin in strong sulphuric acid, and adding water to the solution, a substance is precipitated, resembling hæmatin but not containing iron; it is soluble in alkalis. The solution of this non-ferruginous hæmatin in strong sulphuric acid likewise absorbs blue and violet light strongly; on diluting it with sulphuric acid, a very dark well-defined band appears about midway between D and E; and a narrow band between C and D (near D), the spectrum appearing also very darkly shaded between D and the dark absorption-band. The solution of non-ferruginous hæmatin in dilute ammonia exhibits the smallest absorption for red light; on diluting with water, an absorption-band appears midway between C and D, and three others on further dilution. The absorption of this solution is altered by ammonium sulphide or potassium cyanide in the same manner as that of ferruginous hæmatin (Hoppe-Seyler, *Jahresb.* 1865, p. 667).

Haematin Hydrochloride. Teichmann's Haemin Crystals. $C^{96}H^{142}N^{12}Fe^{2}O^{18}.2HCl$.—This compound is obtained in regular crystals by treating hæmoglobin or metahæmoglobin with common salt and glacial acetic acid. The crystals are rhombic or six-sided plates, dark blue by reflected, dirty brown by transmitted light. They are quite insoluble in water, alcohol, and ether, soluble in acids and alkalis, but decomposed at the same time by all acids excepting hydrochloric and acetic. They may be heated without decomposition to 130°, but burn at a red heat, leaving a residue of iron oxide.

The following mode of preparing these crystals is recommended by J. Gwosden (*Wien. Akad. Ber.* liii. [2] 683; *Jahresb.* 1866, p. 746): Defibrinated blood dried at ordinary temperatures, or the clot of blood cut up and dried, is triturated in the form of powder with $\frac{1}{5}$ pt. of pure potassium carbonate, and the dry mass is digested at 40°–45° with alcohol of 94 p. c. till the resulting dark garnet-red solution no longer becomes deeper in colour. The liquid is then filtered; the residue again treated with alcohol; and the united extracts are mixed with rather more than an equal volume of water, and then with acetic acid sufficient to produce a slight acid reaction. The brown flocculent precipitate thereby produced is collected on a filter, slowly dried (finally at 100°), then triturated with $\frac{1}{8}$ pt. sodium chloride and 20 to 30 pts. glacial acetic acid, and the mixture is digested for some time at 60° till a crystalline mass separates. The whole is then heated to 100° and left to cool, and the crystals are washed on a filter with warm glacial acetic acid, then pressed, dried, and again boiled with water. According to Hoppe-Seyler (*Med.-chem. Unters.* i. 298; *Jahresb.* 1867, p. 805), the process may be advantageously modified as follows: The blood is coagulated by pouring it into alcohol or boiling water; the clot, separated by filtration and still moist, is warmed with alcohol to which a few drops of strong sulphuric acid have been added; the filtered brown solution is mixed with a warm saturated solution of sodium acetate, then immediately neutralised with sodium carbonate; and, in order to promote the separation of the hæmatin (if it has not taken place already), either mixed with water or freed from alcohol by distillation. The precipitate, after being washed on a filter and dried in the air, is ready for treatment with common salt and acetic acid as above.

Detection of Blood-stains.—The formation of hæmin crystals by the action of common salt and glacial acetic acid is quite characteristic of blood, and affords a very delicate indication of its presence. To ascertain whether a spot on linen, cotton, woollen cloth, wood, or metal consists of blood, the stained tissue or wood, or the substance scraped from the metal, may be simply boiled for a few minutes with glacial acetic acid, a few drops of the solution evaporated to dryness at 40°–60°, and the residue examined by the microscope. In operating on fresh still highly coloured spots, or on dried blood, the addition of sodium chloride may be dispensed with, as the blood itself contains sufficient of that substance to produce the reaction; but if the stain is old, or has been partly washed out with water, a small quantity of common salt must be added during the boiling or before the evaporation (Brücke, *Jahresb.* 1857, p. 609; Scriba, Simon, a. Büchner, *ibid.* 1859, p. 706). Or the substance may be triturated as above described with potassium carbonate, then digested with alcohol at 40°–50°, and the evaporated residue treated on the object-stage of the microscope with salt and glacial acetic acid, or with the latter alone (Gwosden, *loc. cit.*). According to Erdmann (*J. pr. Chem.* lxxxv. 1; *Jahresb.* 1862, p. 634), the colouring matter of blood cannot be extracted from dried clay or ferric oxide by glacial acetic acid; but by digesting a portion of dried soil containing blood with water, or in some cases with potash-ley, and treating the filtered solution with chlorine-water, a coagulum is obtained which yields hæmin crystals with salt and acetic acid. In applying the preceding method to the detection of blood in judicial investigations, it is important to remember that, according to the statements of most observers, the blood of the greater number of warm-blooded animals yields hæmin crystals exhibiting the same form and general appearance as those obtained from human blood. Krauss, however, states that the hæmin crystals from human blood are quite distinct in character from those produced from the blood of oxen, sheep, pigs, or poultry (*Jahresb.* 1861, p. 792).

Another very delicate test for blood is afforded by tincture of *guaiacum*, which, in conjunction with hydrogen dioxide, or ozonised oil of turpentine, or other substance capable of yielding ozone, changes the colour of the blood to blue. The same colour is however produced by guaiacum and ozonising substances, with fresh gluten, casein, legumin, gum arabic, and various iron compounds, especially ferric acetate and citrate: hence this reaction is useful only as a verification of other experiments, and cannot be regarded as affording positive demonstration of the presence of blood; its non-production may, however, be accepted as a proof that the spot under examination does not consist of blood (Van Deen, *Zeitschr. anal. Chem.* ii. 459. Liman, *ibid.*; *Jahresb.* 1863, p. 715. See also Taylor, *Guy's Hospital Reports*, 1868).

On the detection of blood by its absorption-spectrum, see H. C. Sorby (*Chem. News* [1865] xi. 186, 194, 232, 256).

BONE. A large number of carefully conducted analyses of the bones of man and other animals by Zaleski (*Med.-chem. Unters.* i. 19; *Jahresb.* 1866, p. 757) have led to the following results: 1. The proportion of organic to inorganic substance is nearly constant. The mean of several analyses gave:

	Man	Ox	Testudo græca	Guinea-pig
Inorganic substance	65·44	67·98	63·05	65·30
Organic "	34·56	32·02	36·95	34·70

2. The proportions of the several constituents of bone-ash (lime, magnesia, phosphoric oxide, carbon dioxide, calcium chloride, and calcium fluoride) exhibit only slight variations, scarcely beyond the limits of analytical error. 100 grms. of ash yielded:

	Man	Ox	Testudo græca	Guinea-pig
Carbon dioxide .	5·734	6·197	5·276	——
Lime . . .	52·965	53·887	52·396	54·025
Magnesia . .	0·521	0·468	0·565	0·483
Phosphoric oxide .	39·019	40·034	38·672	40·381
Chlorine . .	0·183	0·200	——	0·133
Fluorine . .	0·229	0·300	0·204	——
or				
$(PO^4)^2Mg^3$ . .	1·039	1·024	1·357	1·055
$(PO^4)^2Ca^3$ . .	83·889	86·096	85·981	87·379
CaO * . . .	7·648	7·357	6·319	7·027

3. With exception of the bones in the shield of *Testudo græca*, all bones contain

* As carbonate, fluoride, or chloride.

chlorine, in the form of a compound insoluble in cold water.—4. The quantities of chlorine and fluorine in all bones are nearly the same; the latter, however, is less according to these analyses than according to older determinations.—5. The quantity of calcium, not in the form of phosphate, is greater than that which corresponds with the formula of apatite, $(PO^4)^2Ca^3 . CaF^2$.

Experiments with pigeons showed that an increase in the proportion of lime or phosphoric acid in the food does not produce any alteration in the proportion of organic to inorganic substance, or of lime to phosphoric acid.

Roussin (*J. Pharm.* [3] xliii. 102) found that the young of a rabbit which received in its food a small quantity of calcium arsenate contained in their bony skeleton (but not in the muscular tissue) notable quantities of arsenic.

Wicke (*Ann. Ch. Pharm.* cxiii. 251) has examined the ash of the bony plates in the scales of the armadillo (*Dasypus sexcinctus*), and that of the caudal vertebræ, with the following results:

	$(PO^4)^2Ca^3$	$(PO^4)^2Mg^3$	CO^3Ca	SO^4Ca	SiO^2	Fe^2O^3	KCl
Bony plates . .	85·33	1·19	11·75	0·38	0·29	0·65	0·56
Caudal vertebræ .	87·56	2·18	10·36	—	—	0·29	—

Respecting the composition of fossil bones, see Delesse, *Compt. rend.* lii. 728; *Jahresb.* 1861, p. 1087; Couerbe, *Compt. rend.* liv. 49; Göbel, *J. pr. Chem.* lxxxvi. 318; Schwarzenbach, *Chem. Centr.* 1862, p. 706; *Jahresb.* 1862, p. 549;—of bones from Pompeii: De Luca, *Compt. rend.* lix. 567; *Jahresb.* 1864, p. 674.

BONSDORFFITE. The mineral thus named by Thomson, from Abo in Finland, appears from analyses made in Arppe's laboratory to be identical with Fahlunite (*Jahresb.* 1862, p. 748).

BORNEOL, $C^{10}H^{18}O$, is produced, together with sodium-camphor, by the action of sodium on common camphor:

$$3C^{10}H^{16}O + Na^2 = C^{10}H^{18}O + 2C^{10}H^{15}NaO$$

(Baubigny, *Zeitschr. f. Chem.* [2] iii. 71).

Borneol heated with nitric acid yields camphretic acid, $C^{10}H^{14}O^2$, together with camphoric acid, $C^{10}H^{16}O^4$ (Schwanert, *Jahresb.* 1863, p. 400).

Borneol heated with organic acids to 200° forms compound ethers: with stearic acid, for example, it yields the ether $C^{28}H^{52}O^2 = C^{18}H^{36}O^2 + C^{10}H^{18}O - H^2O$. The stearate and benzoate are neutral, colourless, inodorous liquids, soluble in alcohol and in ether, and resolved by alkalis into borneol and the corresponding acids (Berthelot, *Compt. rend.* xlvii. 262).

A solid substance, $C^{15}H^{26}O$, homologous with borneol, is deposited from oil of patchouli (*q.v.*).

BORON. The so-called graphitoïdal boron (i. 628) appears from recent experiments by Wöhler a. Deville (*Ann. Ch. Pharm.* cxli. 268) to consist of aluminium boride, AlB^2 (anal. 54·91 aluminium, 45·09 boron; calc. 55·46 and 44·54). Its formation on fusing aluminium with amorphous boron or boric oxide appears to take place especially when the heat applied is neither very strong nor long-continued. It is also produced when aluminium is fused in vapour of boron chloride. Its crystals, as well as those of adamantine boron, appear from Miller's determinations (*Phil. Mag.* [4] xxxi. 397) to belong to the monoclinic system. When ignited in the air it acquires a steel-grey tarnish, but does not burn; but in chlorine gas it burns with vivid incandescence, yielding aluminium chloride and boron chloride. It is easily dissolved by moderately strong nitric acid; slowly, and with evolution of hydrogen, by hot strong hydrochloric acid and by solution of caustic soda.

Boron Chloride, BCl^3, boils at 18·23° under a pressure of 760 mm. (Regnault, *Jahresb.* 1863, p. 70). It unites with *ethyl cyanide*, forming the compound $C^3H^5N . BCl^3$, which crystallises in right rhombic prisms, may be fused, and for the most part volatilised, without alteration, and is decomposed by water into ethyl cyanide, boric acid, and hydrochloric acid. *Boron bromide* forms a similar compound (Gautier, *Ann. Ch. Pharm.* cxlii. 289).

According to Nicklès (*Bull. Soc. Chim.* [2] iv. 189), a solution of boric oxide in absolute alcohol absorbs hydrochloric acid gas, forming an oily liquid having the composition $3B^2O^3 . 6HCl . 10C^2H^6O$, and yielding by distillation at 85° a compound of boron chloride with ethyl oxide and water, $2BCl^3 . 5C^4H^{10}O . 9H^2O$. A bromine-compound containing $2BBr^3 . 13C^4H^{10}O . 16H^2O$ is obtained in a similar manner. According to Schiff, on the other hand (*Ann. Ch. Pharm. Suppl.* v. 154), an alcoholic solution of boric oxide saturated with hydrochloric acid gas yields, not a compound of boron chloride with ether, but a mixture of ethyl borate, alcohol, ethyl chloride, and hydrochloric acid; in like manner, boron chloride in contact with alcohol forms ethyl borate and hydrochloric acid.

Boron nitride, BN, is easily produced by heating 1 pt. of fused and very finely pulverised boric oxide with 1½ to 3 pts. urea; it always however retains a small quantity of boric oxide, which cannot be removed by washing. It is not altered by moderate ignition in chlorine gas, but acquires thereby the property of glowing very brightly at the edge of a flame. At a very strong red heat, boric chloride is formed. Vapour of iodine and dry hydrogen do not act upon it (Darmstadt, *Ann. Ch. Pharm.* cli. 255).

Boric Oxide, Acid, and **Salts.** According to Merz (*J. pr. Chem.* cxix. 179), crystallised boric acid heated to 270° retains from 2·8 to 3·1 p. c. water, the residue having the composition $8B^2O^3.H^2O$.

A compound of boric oxide with *sulphuric acid*, $5B^2O^3.2H^2SO^4$, is produced by fusing boric oxide in strong sulphuric acid, and heating the clear liquid to 250°-280° till the excess of sulphuric acid is driven off. The compound solidifies on cooling to a transparent glass, which for the most part may be further heated to 350°-400° without decomposition, but sometimes gives off water and sulphuric acid, and is converted into a dry white mass (Merz). Boric oxide is dissolved by *acetic oxide* at the boiling heat, forming a syrupy liquid which solidifies on cooling to a vitreous mass consisting of acetic borate, $B(C^2H^3O)O^3$, which is resolved by water into boric and acetic acids (Schützenberger, *Rép. Chim. pure*, iv. 5).

In estimating boron or boric acid by evaporating the aqueous solution of the acid with a known weight of sodium carbonate, and determining the carbonic acid in the residue (i. 630), the process may be simplified—if the amount of the boric acid is known within certain limits—by so adjusting the quantity of alkaline carbonate added, that for each molecule of boric oxide, B^2O^3, in the solution, there shall be present not less than 1 and not more than 2 molecules of sodium oxide, Na^2O (or between 1 and 2 at. sodium to 1 at. boron). Under these circumstances, the whole of the carbonate is decomposed, the weight of the residue is constant, and the carbonic acid estimation may be dispensed with. To avoid excessive tumefaction and violent evolution of gas, it is best to evaporate the solution in a platinum dish, heat the residue therein till all decrepitation has ceased, and then introduce it by small portions into a red-hot crucible (Schaffgotsch, *Pogg. Ann.* cvii. 427).

Marignac (*Zeitschr. anal. Chem.* i. 405) gives the following method for estimating boric acid in solutions containing only alkali-metals. Insoluble borates must be previously decomposed by fusion with sodium carbonate, and any silica that may be present precipitated from the aqueous solution of the fused product with chloride or carbonate of ammonium. The solution is then to be neutralised with hydrochloric acid, mixed with a quantity of magnesium chloride (or, better, magnesium-ammonium chloride) such that 2 pts. of magnesia may be present for every 1 pt. of boric oxide, and after addition of ammonia (which should produce no turbidity, otherwise sal-ammoniac must be added) evaporated in a platinum dish. The boric acid appears to be present in this solution as magnesium-ammonium borate, and is held in firm combination; nevertheless it is advisable to maintain the alkaline reaction during the evaporation by occasional addition of ammonia. On heating the dried residue to redness, and lixiviating it with boiling water till the chlorine reaction is no longer apparent, the greater part of the boron remains as insoluble magnesium borate, a small portion however passing into the wash-water. The preceding series of operations must therefore be repeated on the entire filtrate; and even the wash-waters then obtained yield small quantities of magnesium borate by further evaporation, ignition, and washing. The whole of the residues thus obtained are ignited together in an open crucible to decompose any magnesium chloride that may be present, then weighed; and the quantity of magnesia in them is determined either by precipitation as ammonio-magnesian phosphate, or alkalimetrically by solution in a known volume of standard sulphuric acid and counter-titration. The quantity of boric oxide is determined by difference.

To decompose borofluorides, Marignac fuses them with alkaline carbonate; dissolves the fused mass in water; decomposes the greater part (not the whole) of the excess of alkaline carbonate by heating with sal-ammoniac; and precipitates the solution with a neutral or ammoniacal solution of calcium chloride. (If the liquid were acidulated, the borofluoride would be reproduced.) The precipitate of calcium carbonate and fluoride is easily washed, after which it is to be dried, gently ignited, mixed with acetic acid and evaporated, and further treated in the usual way. The liquid filtered from the precipitate formed by calcium chloride contains the whole of the boric acid, which, after the excess of lime has been removed by carbonate and oxalate of ammonium, may be estimated in the manner above described.

P. Le Roux (*Bull. Soc. Chim.* [2] vii. 485; *Jahresb.* 1867, p. 137) describes certain peculiar alterations exhibited by fused borates when rapidly cooled.

When boric acid and *alumina* are dissolved together in hydrochloric acid, and the solution is treated with ammonium carbonate, part of the boric acid goes down with the alumina, and can only be separated from it by heating with hydrofluoric acid (Wöhler, *Jahresb.* 1867, p. 836).

A compound of boric and phosphoric oxides, $B^2O^3.P^2O^5$, is formed by heating crystallised boric acid with concentrated aqueous phosphoric acid. It is a white earthy mass, which melts before the blowpipe, is not decomposed by boiling water or by strong acids, but is dissolved by boiling caustic alkalis. By fusion with sodium it yields sodium phosphide and a black scoriaceous mass, probably consisting of boron phosphide (Vogel, *Zeitschr. f. Chem.* vi. 125).

Metallic Borates. *Potassium triborate*, $K^2O.3B^2O^3.5H^2O$ or $2(KBO^2.B^2O^3).5H^2O$, crystallises from a hot solution containing 2 mol. boric oxide to 1 mol. potassium carbonate at 6°, in rhombic prisms having a vitreous lustre and permanent in the air. Combination $\infty P\,.\,\infty\breve{P}\infty\,.\,\breve{P}\infty\,.\,\bar{P}\infty$, with the angles $\infty P : \infty P = 121° 17'$; $\bar{P}\infty : \infty\breve{P}\infty = 132° 38'$; $\breve{P}\infty$; $\bar{P}\infty$ (at the principal axis) $= 60° 16'$. Ratio of axes $a : b : c = 0{\cdot}5315 : 1 : 0{\cdot}9206$. *Rubidium biborate*, $Rb^2O.2B^2O^3.6H^2O$ or $2RbBO^2.B^2O^3.6H^2O$, separates in like manner from a hot solution of 2 mol. B^2O^3 to 1 mol. Rb^2CO^3 at 6°, in small tabular rhombic crystals, exhibiting the combination $oP\,.\,\infty P\,.\,\infty\breve{P}\infty$, with the angles $\infty P : \infty P = 82° 23'$; $\infty P : \infty\breve{P}\infty = 131° 4'$. It is permanent in the air, has an alkaline taste, and is more soluble in hot than in cold water (Reissig, *Ann. Ch. Pharm.* cxxvii. 33).

Neutral sodium borate, $NaBO^2.4H^2O$, crystallises, according to Hahn (*Arch. Pharm.* [2] xcix. 146), in monoclinic combinations, $-P\,.\,\infty P\,.\,oP\,.\,\infty P\infty\,.\,(\infty P\infty)$, with the angles $\infty P : \infty P$ (clinod.) $= 87°$; $\infty P\infty : oP = 106° 41'$; $oP : -P = 138° 57'$. Twins often occur combined by the face $\infty P\infty$; cleavage imperfect parallel to $\infty P\infty$.

According to A. Vogel (*Jahresb.* 1867, p. 191), crystallised borax, $Na^2O.2B^2O^3.10H^2O$, is soluble in 14·7 pts. of glycerin.

Copper Borates.—On adding borax to a solution of cupric sulphate, a basic sulphate $7CuO.2SO^3 + 8H^2O$ is precipitated in the first instance, and with excess of borax, a cupric borate $5CuO.2B^2O^3 + 12H^2O$. A solution of equivalent quantities of cupric acetate and borax in ammonia mixed with about half its volume of absolute alcohol, gradually deposits dark blue microscopic rhombic tables of the salt $CuO.2B^2O^3.4NH^3 + 6H^2O$. The same salt is obtained by dissolving 1 mol. cupric acetate in ammonia, adding 2 mol. boric oxide, warming the liquid till the precipitate dissolves, and leaving it to cool. It smells strongly of ammonia, effloresces in contact with the air, dissolves in dilute acids, and is resolved by boiling with water into ammonia and cupric borate (E. Pasternack, *Ann. Ch. Pharm.* cli. 116).

Magnesium Borate.—A mixture of anhydrous magnesium chloride and a large quantity of sodium chloride, with addition of boric oxide and magnesia, subjected in a platinum crucible to the strongest heat of an air-furnace, and then left to cool as slowly as possible, yields a mass which, when exhausted with water, leaves a crystalline powder appearing under the microscope as a mixture of monometric and prismatic crystals. On leaving this mass for several days in contact with cold concentrated hydrochloric acid, the prismatic crystals (probably consisting of a mixture of $MgO.B^2O^3$ and $2MgO.B^2O^3$) dissolve, leaving regular crystals of the compound $MgCl^2.2(3MgO.4B^2O^3)$, which exhibit the forms $\left(O \text{ and } \frac{O}{2}\right)$, and the pyroelectric properties of native boracite (Heintz a. Richter, *Pogg. Ann.* cx. 613).

Zinc Borates.—Borax reacts with zinc sulphate in the same manner as with copper sulphate, throwing down first a basic sulphate, afterwards a borate containing 38·58 p. c. ZnO and 36·55 water. On dissolving 4 pts. of this zinc borate and 5 pts. boric oxide in ammonia, and covering the solution with a layer of alcohol, the salt $ZnO.2B^2O^3.4NH^3 + 6H^2O$ is deposited in efflorescent rhombic prisms, soluble in ammonia and in dilute acids. The same salt is produced by dissolving zinc acetate obtained from 20 grms. of basic zinc carbonate, and 38 grms. boric oxide in ammonia at a gentle heat, and mixing the cooled liquid with alcohol (E. Bäscher, *Ann. Ch. Pharm.* cli. 235).

Boric Ethers (Schiff a. Bechi, *Bull. Soc. Chim.* [2] v. 372; vi. 36. Schiff, *Giornale di Scienze naturali ed economiche di Palermo*, v. 9).—The tri-alcoholic borates were first prepared in 1846 by Ebelmen and Bouquet, who obtained them by the action of boron trichloride on the respective alcohols (i. 649). H. Rose, in 1856, gave an easier mode of preparing them by the dry distillation of a mixture of potassium ethylsulphate and anhydrous borax; and this method was perfected by Frankland, in connection with his researches on the action of zinc-ethyl and zinc-methyl on triethylic borate (ii. *525*). With regard to the preparation of the non-saturated boric ethers, Ebelmen, in 1855, published a research relating to the action of boric oxide or anhydride upon the alcohols, and he there describes a number of vitreous boric ethers, which he derives from a hydrate, $B^4H^2O^7$, corresponding to borax. These however appear, from the experiments of Schiff, to have been nothing but mixtures, the supposed diethylic tetraborate, $B^4(C^2H^5)^2O^7$, for example, being a mixture of monethylic borate, $B(C^2H^5)O^2$, and monethylic triborate, $B^3(C^2H^5)O^5$.

When equal weights of pulverised boric oxide and absolute alcohol are mixed together, the temperature of the mixture rises considerably, and after eight or ten hours the alcohol is completely absorbed by the boric oxide, which partly becomes hydrated and converted into a white spongy mass. If the mixture, contained in a flask furnished with a long tube, be now raised to ebullition, a large part of the boric acid dissolves, and on then adding a little alcohol the whole may be easily made to enter into solution. As the liquid cools, a white mammellated crystalline mass separates, consisting of boric trihydrate, BH^3O^3. The colourless or slightly yellow liquid, separated from the crystals and distilled, leaves a small vitreous residue, consisting of a boric ether (or rather a mixture of two such ethers), while the distillate contains a much larger quantity of a boric ether, which was supposed by Ebelmen to be the vitreous ether just mentioned mechanically carried forward by the alcohol. According to Schiff, however, it consists of triethylic borate or ethylic orthoborate, a considerable quantity of which passes over between 110° and 130°. From these results it appears that the reaction between absolute alcohol and boric oxide is that which is represented by the equation:

$$B^2O^3 + 3C^2H^5HO = BH^3O^3 + B(C^2H^5)^3O^3.$$

This, according to Schiff, is the easiest and most economical method of preparing triethylic borate.

The best way of separating the boric ether from the alcohol which distils over with it, is to mix the distillate with strong sulphuric acid, whereby two strata of liquid are formed, the upper consisting mainly of triethylic borate, which may be further purified by rectification.

Triethylic Borate is a limpid, very mobile liquid, which burns without a wick, with a green flame, exhaling vapours of boric acid. It boils at 120° under a pressure of 760 mm. (with the thermometer in the vapour, and pieces of platinum in the liquid). Sp. gr. 0·861 at 26·5°, and 0·887 at 0°: hence one volume of the liquid at 0° gives 1·033 vol. at 26·5°, an expansion nearly equal to that of ethylic acetate, propionate, and nitrate. It tastes like boric acid and alcohol together, and smells like the latter, the effect on the organs of taste and smell being evidently due to decomposition of the ether. The bitter taste and pungent aromatic smell attributed to this ether by Ebelmen and Bouquet and by Bowman were probably due to some chlorinated products of the ethylic group, arising from the chloride of boron used by them in the preparation. The ether is easily decomposed by atmospheric moisture, and a small quantity suffers decomposition at each distillation, probably in consequence of the presence of moisture in the vessel, the latter portions often exhibiting a higher boiling point, and ultimately leaving a resinous residue.

Triethylic borate heated to 160°–180° in a sealed tube with boric hydrate, BH^3O^3, is decomposed, partly according to the equation:

$$\underset{\substack{\text{Triethylic}\\\text{borate}}}{B(C^2H^5)^3O^3} + \underset{\substack{\text{Trihydric}\\\text{borate}}}{2BH^3O^3} = \underset{\substack{\text{Monohy-}\\\text{dric borate}}}{3BHO^2} + \underset{\text{Alcohol;}}{3C^2H^6O}$$

partly in the following manner:

$$\underset{\substack{\text{Triethylic}\\\text{borate.}}}{B(C^2H^5)^3O^3} + \underset{\substack{\text{Trihydric}\\\text{borate.}}}{BH^3O^3} = \underset{\substack{\text{Monethylic}\\\text{borate.}}}{B(C^2H^5)O^2} + \underset{\substack{\text{Monohy-}\\\text{dric borate.}}}{BHO^2} + \underset{\text{Alcohol.}}{2C^2H^6O}$$

These decompositions take place also in the above-described preparation of triethylic borate when the temperature is allowed to rise above 130°.

Strong sulphuric acid easily dissolves triethylic borate, and if the mixture be heated, water and ethylene gas are given off; and if water be then added before the temperature rises higher, sulphurous oxide is given off, monohydric borate separates, and ethyl-sulphuric acid is found in the liquid:

$$B(C^2H^5)^3O^3 + SH^2O^4 = S(C^2H^5)HO^4 + 2C^2H^4 + BHO^2 + H^2O.$$

If water be added, drop by drop, to the solution of boric ether in sulphuric acid heated to 140°–150°, trihydric borate is likewise deposited, but at the same time vapour of ethylic oxide separates, and the liquid contains ethyl-sulphuric acid:

$$B(C^2H^5)^3O^3 + SH^2O^4 + H^2O = S(C^2H^5)HO^4 + BH^3O^3 + (C^2H^5)^2O.$$

If an acid be added instead of water, the corresponding compound ether is formed, instead of ethylic oxide; thus, with benzoic acid at 120°:

$$B(C^2H^5)^3O^3 + SH^2O^4 + C^7H^6O^2 = S(C^2H^5)HO^4 + BH^3O^3 + 2C^7H^5(C^2H^5)O^2.$$

A similar reaction takes place with other acids, as for example with acetic, butyric, and valerianic acids. In other cases triethylic borate etherifies directly; thus it dissolves, with rise of temperature, in nitric acid, and after a while ethylic nitrate is given off, while the liquid becomes filled with crystals of boric acid:

$$B(C^2H^5)^3O^3 + 3NHO^3 = BH^3O^3 + 3N(C^2H^5)O^3.$$

Acetic acid decomposes triethylic borate in a similar manner; so likewise do benzoic and succinic acids when heated with it in sealed tubes to 180°–200°. This mode of preparing compound ethers by means of triethylic borate may, in many cases, be preferable to the somewhat expensive process of decomposing the silver salts of the corresponding acids with ethylic iodide. Oxalic acid acts at 151°; hydrochloric and sulphurous acids may be heated with triethylic borate to 120°–140°, without producing any reaction.

Chlorine, bromine, and iodine act upon triethylic borate, taking the place of part of the hydrogen. The vapour of the ether, mixed with chlorine, takes fire and burns, leaving a carbonaceous residue. The liquid ether rapidly absorbs chlorine, forming a yellow jelly containing more than two atoms of chlorine, but not enough to form the compound $B(C^2H^4Cl)^3O^3$.

Phosphoric pentachloride at ordinary temperatures acts upon triethylic borate in such a manner as to form phosphoric oxychloride, ethyl chloride, and monethylic borate:

$$2B(C^2H^5)^3O^3 + 2PCl^5 = 2POCl^3 + 4C^2H^5Cl + 2B(C^2H^5)O^2.$$

At higher temperatures, boric oxide and ethyl oxide are formed instead of monethylic borate:

$$2B(C^2H^5)^3O^3 + PCl^5 = POCl^3 + 2C^2H^5Cl + B^2O^3 + 2(C^2H^5)^2O.$$

Heated with antimonic chloride, triethylic borate yields antimonic oxychloride, ethyl chloride, ethyl oxide, and monethylic borate:

$$2B(C^2H^5)^3O^3 + SbCl^5 = SbOCl^3 + 2C^2H^5Cl + (C^2H^5)^2O + 2B(C^2H^5)O^2.$$

Monethylic Borate or *Ethylic Metaborate.* $B(C^2H^5)O^2$.—If the crude product of the action of alcohol on boric oxide be fractionally distilled till the vapours exhibit a temperature of 140°–150°, and a sufficient time be allowed to elapse between the collection of the separate fractions to let the boric acid crystallise out, a syrupy, more or less yellow liquid will be obtained on cooling, which after a time deposits a small quantity of boric acid. This liquid is monethylic borate, slightly contaminated with triethylic borate and boric acid. It appears to be formed by the action of boric acid (see above), or of boric oxide, on triethylic borate:

$$B(C^2H^5)^3O^3 + B^2O^3 = 3B(C^2H^5)O^2.$$

Monethylic borate is a dense inodorous liquid, having at 120° the consistence of fuming sulphuric acid. It attracts moisture from the air, and is decomposed into alcohol and boric acid. When directly decomposed by water, it evolves great heat; hence also it feels very hot when placed upon the tongue. It cannot be distilled without alteration. Introduced into a flame on the end of a wire, it burns with a green light, leaving boric acid mixed with charcoal. With alcohol, it forms triethylic borate and boric acid:

$$3B(C^2H^5)O^2 + 3C^2H^5OH = 2B(C^2H^5)^3O^3 + BH^3O^3.$$

Heated with potassium ethylate, it yields potassium borate and triethylic borate:

$$2B(C^2H^5)O^2 + C^2H^5KO = BKO^2 + B(C^2H^5)^3O^3.$$

It is decomposed by acids, but much less easily than triethylic borate, the reaction requiring a temperature of 180°–200°. With acetic acid the action is:

$$B(C^2H^5)O^2 + C^2H^4O^2 = BHO^2 + C^2H^3(C^2H^5)O^2.$$

Monethylic triborate, $B^3(C^2H^5)O^5$, is produced, together with the triethylic ether, by the decomposition of monethylic monoborate at high temperatures:

$$4B(C^2H^5)O^2 = B(C^2H^5)^3O^3 + B^3(C^2H^5)O^5.$$

When monethylic monoborate is heated to 270°–280°, triethylic borate is given off, and the residue cools to a solid mass, which is to be broken up and digested with anhydrous ether; the solution filtered and evaporated leaves the ethylic triborate in the form of a mass resembling gum-arabic. When exposed to the air, it attracts moisture and becomes covered with a crust of boric acid. In water it decomposes rapidly, with evolution of heat. In a gas-flame it burns with a green light, leaving boric oxide mixed with carbon. It is not sensibly altered by heating to 300°. Absolute alcohol reacts with it in the same manner as with monethylic borate, but less energetically, the action requiring a high temperature to complete it:

$$3B^3(C^2H^5)O^5 + 12C^2H^5OH = 5B(C^2H^5)^3O^3 + 4BH^3O^3.$$

Methylic Borates.—The *trimethylic ether*, $B(CH^3)^3O^3$, is prepared, like the corresponding ethyl-compound, by heating boric oxide with methylic alcohol to 100°, then distilling and treating the distillate with strong sulphuric acid, whereby two strata of liquid are formed, the upper containing the trimethylic borate. Schiff, however, did not obtain it pure. The specific gravity of his product was 0·915 at 20°, and 0·940 at 0°. Ebelmen and Bouquet found the density to be 0·955 at 0° for an ether boiling at 72°. The reactions of this ether are analogous to those of triethylic borate. It burns with a flame green throughout, whereas that of triethylic borate is colourless in the middle, the difference arising mainly from the larger proportion of boron in the methylic ether. For this reason, as originally pointed out by Ebelmen, it is better, in testing for boron by the colour of its flame, to use methylic instead of ethylic alcohol.

Monomethylic borate, $B(CH^3)O^2$, is prepared from the preceding compound in the same manner as the monethylic from the triethylic ether. It is much less mobile than the monethylic borate, but resembles the latter in all its chemical reactions. It begins to decompose at 160°, giving off trimethylic borate; and at 250° there remains a mass which, when purified, after cooling, with anhydrous ethyl oxide, exhibits the composition of *methylic triborate*, $B^3(CH^3)O^5$, or $B(CH^3)O^2.B^2O^3$. This ether colours flame green, forms trimethylic borate when heated with methylic alcohol, and is decomposed by water into monomethylic borate and boric acid.

The ether $B^4(CH^3)^2O^7$, described by Ebelmen, appears to have been a mixture of monomethylic borate and triborate.

Amylic Borates.—The *triamylic* and *monamylic* ethers were prepared similarly to the corresponding ethyl-compounds. The former may also be produced by decomposing triethylic borate with amylic alcohol at 160°–180°; but other ethers are formed at the same time, and the purification of the triamylic ether is difficult. This ether boils, according to Schiff, at 254° with the barometer at 760 mm. Ebelmen and Bouquet give 270°–275°, but they state that their determination was made with only a small quantity of impure substance. The reactions of this ether resemble those of the corresponding ethyl-compound, but it burns only with the aid of a wick, and the flame exhibits a green colour only at the base near the wick.

The *monamylic ether* $B(C^5H^{11})O^2$, obtained by heating the crude product of the action of boric oxide on amylic alcohol to 290°, has a density of 0·949 at 20°, and 0·971 at 0° It is much more fluid than the corresponding ethyl and methyl compounds, and burns like the triamylic ether. It sustains a temperature of 300° without sensible alteration, but above that temperature it decomposes, a mixture of mono- and tri-amylic borate distilling over, and a vitreous mass being ultimately left, consisting of *amylic triborate*, $B^3(C^5H^{11})O^5$, mixed with boric oxide, charcoal, and other impurities. Monamylic borate may also be prepared by the action of boric oxide on triamylic borate; and, on the other hand, the action of amylic alcohol on monamylic borate yields the triamylic compound:

$$3B(C^5H^{11})O^2 + 3C^5H^{12}O = 2B(C^5H^{11})^3O^3 + BH^3O^3.$$

Mixed Boric Ethers.—These ethers may be prepared by treating a mono-alcoholic borate with an alcohol different from that whose radicle is contained in the ether. Thus with monethylic borate and amylic alcohol are obtained the following:

$$3BEtO^2 + 3AmHO = BEtAm^2O^3 + BEt^2AmO^3 + BH^3O^3.$$

At the same time, however, another reaction takes place, producing the simple trialcoholic borates, though in quantity smaller than that of the mixed ethers:

$$3BEtO^2 + 3AmHO = BEt^3O^3 + BAm^3O^3 + BH^3O^3.$$

The several products are separated by fractional distillation.

Ethyl-diamylic borate, $B(C^2H^5)(C^5H^{11})^2O^3$, boils at 210°–215°, has a density of

0·852 at 28°, and 0·876 at 0°. It burns, like triamylic borate, only with a wick, but with a more deeply coloured flame. *Amylo-diethylic borate*, $B(C^5H^{11})(C^2H^5)^2O^3$, boils at about 172°–175°, and has a density of 0·858 at 26°; burns without a wick, but not so easily as triethylic borate. These two mixed ethers act chemically like the other trialcoholic borates. An excess of amylic alcohol acts upon them at 160°–180°, with elimination of ethylic alcohol, and formation of triamylic borate: this explains the presence of a rather large proportion of triamylic borate in the product of the reaction of amylic alcohol on monethylic borate. The following equation embraces all the products which this reaction has yielded:

$$7BEtO^2 + 7AmHO = EtHO + BEt^3O^3 + BAmEt^2O^3 + BAm^2EtO^3 + BAm^3O^3 \\ + BAm^3O + 2BH^3O^3.$$

Altogether, the reaction of alcohols on the mono-alcoholic borates is very complicated; and for the further consideration of the products we must refer to the paper cited at the head of this article.

Cetylic Borate. $B(C^{16}H^{33})O^2$.—The action of boric oxide on cetylic alcohol differs from that which it exerts on the lower alcohols of the series, in this respect, that the water eliminated by the reaction, instead of uniting with the boric oxide to form boric acid, is set free in the liquid state, the difference apparently depending upon the higher temperature at which the action takes place. The boric oxide in excess is introduced in small lumps, together with the cetylic alcohol, into a short-necked retort, and heated as long as water separates. The fused mass is then decanted, digested when cold with anhydrous ether, and the decanted solution is evaporated. In this manner, *monocetylic borate*, $B(C^{16}H^{33})O^2$, is obtained, as a white or yellowish mass resembling cetylic alcohol, but somewhat less crystalline; it melts at 58°. The fused substance is permanent in dry air; slowly decomposed by moist air and by cold water, quickly by hot water. It is scarcely inflammable, even with the aid of a wick; dissolves but slightly in benzol. The mode of its formation may be thus expressed:

$$B^2O^3 + 2C^{16}H^{34}O = 2B(C^{16}H^{33})O^2 + H^2O.$$

The other cetylic borates have not been obtained.

Glyceric Borate. $B'''(C^3H^5)'''O^3$.—Coarsely pounded boric oxide dissolves, with elimination of aqueous vapour, in anhydrous glycerin heated to 200°; and if the mixture be kept hot as long as aqueous vapour continues to escape, two molecules of glycerin will dissolve one molecule of boric acid, forming glyceric borate, according to the equation:

$$2(C^3H^5)H^3O^3 + B^2O^3 = 2B(C^3H^5)O^3 + 3H^2O.$$

The fused mass separated by decantation from the unaltered boric oxide forms, on cooling, a pale yellow, horny, transparent substance, very hygroscopic, insoluble in ether, benzol, and chloroform. It dissolves in absolute alcohol without alteration, a property which shows it to be a saturated compound, inasmuch as all the unsaturated boric ethers are decomposed by alcohol. The alcoholic solution, evaporated at 50°–60°, leaves the glyceric borate unaltered; but if the compound be heated to 120° in a sealed tube with absolute alcohol, it is decomposed in the manner shown by the equation:

$$B(C^3H^5)O^3 + 3C^2H^6O = B(C^2H^5)^3O^3 + C^3H^8O.$$

Glyceric borate dissolves without alteration in a small quantity of cold water; but on heating it, the dense, somewhat acid solution suddenly coagulates to a dense mass, and acquires a sweet taste, being in fact resolved into boric hydrate and glycerin. It has no fixed melting point, but behaves like a vitreous substance, gradually softening at about 170°. Ammonia gas does not act upon it, unless moisture is present, in which case a gelatinous mass is formed, containing ammonia borate. Strong sulphuric acid blackens glyceric borate even at 100°.

From the observations of Schützenberger (*Compt. rend.* liii. 538), it appears that boric oxide and *acetic oxide* unite directly in the proportion of B^2O^3 to $C^4H^6O^3$, forming a vitreous substance, which is decomposed by water into boric and acetic acids, and therefore consists of *acetic borate*, $B(C^2H^3O)O^2$.

Phenylic Borates.—Boric oxide acts upon phenol at high temperatures in the same manner as on cetylic alcohol and glycerin, giving rise to direct elimination of water, producing however not merely one, but several boric ethers. When two parts of boric oxide are heated with three parts of phenol, and the mixture is cooled after reacting for half an hour, a syrupy liquid is obtained, from which ether extracts monophenylic borate, $B(C^6H^5)O^2$:

$$B^2O^3 + C^6H^6O = B(C^6H^5)O^2 + BHO^2.$$

As thus prepared, however, it is very impure. A purer product is obtained by heating phenylic triborate to 150° with ethylic alcohol, whereby monophenylic borate is produced, together with triethylic borate and boric acid:

$$B^3(C^6H^5)O^5 + 3C^2H^6O = B(C^6H^5)O^2 + B(C^2H^5)^3O^3 + BH^3O^3.$$

The product is freed from triethylic borate by distillation, ultimately at 180°, and the monophenylic borate is extracted from the residue by solution in ether and evaporation. Thus obtained, it is a yellow substance having a faint odour and the consistence of turpentine.

Phenylic triborate, $B^3(C^6H^5)O^5$, is formed when phenol is boiled for several hours with boric oxide in a flask fitted with a condensing tube; an additional quantity of boric oxide then dissolves, and lastly also the boric hydrate formed at the commencement of the action, together with the monophenylic ether, in the manner shown by the last equation but one. The phenylic triborate is produced by the reaction of this boric hydrate and the oxide on the phenylic monoborate, thus:

$$2B(C^6H^5)O^2 + 2BHO^2 + B^2O^3 = 2B^3(C^6H^5)O^5 + H^2O.$$

Phenylic triborate, when freed from excess of boric acid by means of anhydrous ether, forms an orange-coloured vitreous mass, having a faint odour and internally the aspect of amber. It is slowly decomposed by moist air and cold water, quickly by hot water and dilute aqueous alkalis. Alcoholic potash scarcely attacks it, probably because potassium borate is insoluble in alcohol. It is almost insoluble in benzol, chloroform, and carbon bisulphide; begins to soften at about 80°, but does not exhibit any definite melting point. The alcoholic solution is not coloured violet by ferric chloride. The triborate dissolves in hot strong sulphuric acid; and on adding water, boric acid is deposited, and a solution of phenylsulphuric acid is obtained:

$$B^3(C^6H^5)O^5 + SH^2O^4 + 4H^2O = S(C^6H^5)HO^4 + 3BH^3O^3.$$

With hot nitric acid, it yields boric and picric acids:

$$B^3(C^6H^5)O^5 + 3NHO^3 + 2H^2O = C^6H^3(NO^2)^3O + 3BH^3O^3.$$

Tetraphenylic diborate, $B^2(C^6H^5)^4O^5$, is produced, together with phenylic triborate, when monophenylic monoborate is heated to temperatures above 350°:

$$5B(C^6H^5)O^2 = B^3(C^6H^5)O^5 + B^2(C^6H^5)^4O^5.$$

To complete the reaction, the temperature must be raised considerably above the boiling point of mercury. The yellow oil which passes over on distillation is rectified, and that which distils above 300° is collected apart. The tetraphenylic ether is also formed, together with ethylic phenate and common alcohol, by heating triethylic borate to 160°–180° in a sealed tube with phenol:

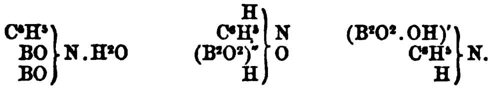
$$2B(C^2H^5)^3O^3 + 5C^6H^6O = B^2(C^6H^5)^4O^5 + C^6H^5(C^2H^5)O + 5C^2H^6O.$$

Tetraphenylic diborate is a greenish-yellow oil, having a faint odour of phenol, a density of 1·100 at 20°, and 1·124 at 0°, at which latter temperature it has the consistence of castor oil. Its boiling point is above that of mercury. At each distillation it undergoes partial decomposition, leaving a residue of phenylic triborate. It is quickly decomposed by water. With strong sulphuric acid it forms a red-brown solution, which, when heated and poured into water, forms a deposit of boric acid and a solution of phenylsulphuric acid:

$$B^2(C^6H^5)^4O^5 + 4SH^2O^4 + H^2O = 4S(C^6H^5)HO^4 + 2BH^3O^3.$$

There are no mixed boric ethers containing phenyl.

BORIC ANILIDE. $B^2O^3.C^6H^7N$.—Aniline does not unite directly with boric oxide or boric hydrate, neither does it decompose the trialcoholic boric ethers when heated therewith; but when it is mixed with monethylic or monomethylic borate, the liquid becomes hot, and is transformed into a resinous mass which becomes pulverulent when treated with anhydrous ether. This mass contains the elements of boric oxide and aniline, and may be regarded as *hydrated diboric anilide*, or as *boranilic acid*, according to the formulæ:



$$\left.\begin{array}{r}C^6H^5\\BO\\BO\end{array}\right\}N.H^2O \qquad \left.\begin{array}{r}H\\C^6H^5\\(B^2O^2)''\\H\end{array}\right\}\begin{array}{l}N\\O\end{array} \qquad \left.\begin{array}{r}(B^2O^2.OH)'\\C^6H^5\\H\end{array}\right\}N.$$

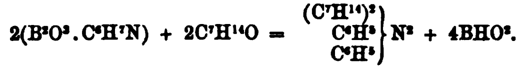
Its formation is represented by the equation:

$$3B(C^2H^5)O^2 + C^6H^7N = B^2O^3.C^6H^7N + B(C^2H^5)^3O^3.$$

Boric anilide is a white, inodorous substance, as light as magnesia, and unalterable in dry air, if it has been thoroughly washed with ether. Water decomposes it immediately into aniline and boric acid. Alcohol dissolves it readily, and leaves it on evaporation in the form of a gummy mass; but when heated in a sealed tube with alcohol to 120° it is resolved into aniline, triethylic borate, and boric acid:

$$B^2O^3.C^6H^7N + 3C^2H^6O = B(C^2H^5)^3O^3 + BH^3O^3 + C^6H^7N.$$

It dissolves in strong sulphuric acid, forming a red-brown liquid, which blackens at a slightly elevated temperature without evolution of gas. The alcoholic solution of the anilide mixed with oxalic acid, also in alcoholic solution, yields a precipitate of aniline oxalate unmixed with boric acid; with platinic chloride also a precipitate of pure aniline platinochloride is obtained. With aldehydes it reacts like free aniline, forming diamides; thus with œnanthol:



$$2(B^2O^3.C^6H^7N) + 2C^7H^{14}O = \left.\begin{matrix}(C^7H^{14})^2\\ C^6H^5\\ C^6H^5\end{matrix}\right\}N^2 + 4BHO^2.$$

Heated to 110°, it gives off water, and leaves a gummy amorphous body, which, when pure, probably consists of $N(BO)^2(C^6H^5)$.

The action of monethylic borate on *ammonia* dissolved in anhydrous ether is not analogous to its reaction with aniline, the product containing at least 2 mol. B^2O^3 to 1 mol. NH^3. The white flocculent substance when heated gives off ammonia and water, and if the residue be exhausted with boiling water, a white powder is left, consisting of *boron nitride*:

$$B^2O^3 + 2NH^3 = 2BN + 3H^2O.$$

Boric oxide heated in a current of dry ammonia gas is also partially converted into boron nitride; but the quantity of this substance formed in either case is but small.

BORONATROCALCITE. This name, as well as *Hydroborocalcite*, *Hayesin*, and *Tiza*, is applied to a mineral composed of the borates of calcium and sodium, found chiefly in the province of Tarapaca in Peru, and now extensively used for the manufacture of boric acid and the alkaline borates. It occurs in nodular masses of fibrous structure, often mixed with glauberite and common salt. The numerous analyses of the mineral—even when it is freed as far as possible from these admixtures—exhibit great diversities of composition, so that several formulæ have been assigned to it. Rammelsberg (*Mineralchemie*, p. 252) regards it as $(Na^2O.2B^2O^3) + 2(CaO.B^2O^3) + 18aq.$, or $(Na^2O.2B^2O^3.10aq.) + 2(CaO.2B^2O^3.4aq.)$, i.e. as 1 mol. of borax combined with 2 mol. of the borocalcite. Phipson (*Chem. News*, iv. 182) gives the formula $(Na^2O.2B^2O^3.10aq.) + 2(CaO.B^2O^3.2aq.) + 2aq.$ Kraut (*Arch. Pharm.* [2] cxii. 25) gives $(Na^2O.2B^2O^3) + (2CaO.3B^2O^3) + 15aq.$; and Lunge (*Ann. Ch. Pharm.* cxxxviii. 56), from his analysis of a specimen from Chile, deduces the formula

$$2(Na^2O.2B^2O^3) + 5\left(\left.\begin{matrix}CaO\\ MgO\end{matrix}\right\}.2B^2O^3\right) + 12aq.$$

For analyses, see *Jahresbericht f. Chem.* 1849, p. 799; 1853, p. 852; 1854, p. 867; 1856, p. 884; 1857, p. 697; 1858, p. 737; 1859, p. 816; 1861, p. 1028; 1862, p. 759; 1866, p. 953; also, Richardson and Watts's *Chemical Technology*, pt. iv. pp. 209–211.

BOTALLACKITE. See COPPER OXYCHLORIDES.

BOURBOULITE. This name is given by Lefort (*Compt. rend.* lv. 919) to a blue ferroso-ferric sulphate found, together with larger quantities of a greenish-yellow salt of similar composition, in the pyritiferous pumice-tufas of Bourboule (Puy-de-Dôme). The blue salt is regarded by Lefort as identical with the salt $3(FeO.SO^3) + 2(Fe^2O^3.SO^3)$ artificially prepared by Barreswil.

BOURNONITE. Cu^1PbSbS^3 or $Cu^2S.2PbS.Sb^2S^3$.—The primary form of this mineral is an orthorhombic prism of 93° 40′; $oP : \bar{P}\infty = 138° 6'$. Axes $a : b : c = 0{\cdot}662 : 1 : 0{\cdot}95618$. For details of the crystalline form, see Zirkel, *Jahresb.* 1862, p. 711; Hessenberg, *ibid.* 1865, p. 798.

BRAGITE. The greyish-brown mineral from Arendal in Norway thus named by Forbes a. Dahll (i. 657) appears, from an analysis by J. A. Michaelson (*J. pr. Chem.* xc. 108; *Jahresb.* 1863, p. 830), to be a niobate of yttrium, and identical with tyrite and fergusonite. (See NIOBIUM, iv. 55.)

BRASSIDIC ACID. $C^{22}H^{42}O^2$.—An acid standing to erucic acid in the same relation as elaïdic to oleic acid. It is obtained by heating erucic acid with dilute nitric acid to 60°–70°, till gas begins to escape, and then cooling the mixture. The solidified product recrystallised from alcohol yields brassidic acid in white laminæ, melting at 66°, and solidifying again in the crystalline form at 54°. Brassidic acid is a strong monobasic acid, less soluble in alcohol and ether than erucic acid; its alcoholic solution reddens litmus-paper. The *sodium salt* $C^{22}H^{41}NaO^{2}$ crystallises from alcohol in laminæ, which easily become electric by friction, like those of the acid, and do not melt till heated above 200°. The *potassium salt* crystallises in scales; the *magnesium salt* may be crystallised from alcohol. The *barium*, *calcium*, *lead*, and *silver salts* are insoluble in water and in alcohol.

Brassidic acid, like erucic acid, unites with 1 mol. of bromine, forming brassidic acid bromide, $C^{22}H^{42}O^{2}Br^{2}$, which separates from alcohol in small colourless crystals melting at 54° and solidifying at 38°–40°. It is attacked at 210° by alcoholic potash, which abstracts 2HBr, and converts it into benolic acid, $C^{22}H^{40}O^{2}$. When left in contact for eight or ten days with sodium-amalgam, it gives up all its bromine, reproducing brassidic acid (Hausknecht, *Ann. Ch. Pharm.* cxliii. 40).

BRASSYLIC ACID. $C^{11}H^{20}O^{4}$.—This acid, homologous with oxalic acid, is produced, together with the corresponding aldehyde and dioxybenolic acid, by the action of fuming nitric acid on benolic acid (p. 257). On subjecting the yellow oil which separates from the alcoholic mother-liquor of benolic acid to distillation with steam, brassylic aldehyde, $C^{11}H^{20}O^{3}$, passes over as a pungent oil, and the residue in the retort solidifies to a network of crystals consisting of benolic, dioxybenolic, and brassylic acids. The last-mentioned acid is obtained pure by leaving either the crude or the distilled oil under bromine and water for several days, and recrystallising the solid acid thereby produced from hot water. Brassylic acid melts at 108·5° and solidifies at 105°. It is nearly insoluble in cold water, slightly soluble in boiling water, easily in alcohol and ether. It is formed from the aldehyde by simple addition of oxygen; also, perhaps together with other acids of the same series, by the action of red fuming nitric acid on erucic acid. It is bibasic. The brassylates of the alkali-metals are soluble in water; the *sodium* and *ammonium salts* crystallise in nodules; the *calcium salt* contains $C^{11}H^{18}CaO^{4}.3H^{2}O$; the *silver salt* $C^{11}H^{18}Ag^{2}O^{4}$ turns violet on exposure to light (Hausknecht, *loc. cit.*).

BRAYERA ANTHELMINTICA. The flowers of this plant, mixed with the peduncles and fragments of the leaves, constitute the drug called *Kusso* or *Kousso*, which is used as a remedy for tape-worm. Pavesi (*J. Pharm. d'Anvers*, Oct. 1858; *Jahresb.* 1859, p. 585) attributes the anthelmintic action of the drug to a substance, called kussin or taenin, which he prepares by repeatedly digesting the kusso, mixed with slaked lime, in alcohol of 60°–70° p. c., boiling the residue with water, uniting the filtered extracts, distilling off the alcohol, and mixing the aqueous residue with a slight excess of acetic acid. The kussin, purified by solution in alcohol and treatment with animal charcoal, and precipitated from the concentrated alcoholic solution by water, is a brittle resin having a dark yellow colour in powder, a slightly bitter taste, like that of kousso itself, soluble in alkalis, not in acids, melting at 100°, and decomposing at a higher temperature. It amounts to 4 p. c. of the kusso. According to C. Bedall (*Chem. Centr.* 1863, p. 124), kussin melts, with decomposition, at 193°–195°. It is not a glucoside. Its formula is $C^{26}H^{44}O^{5}$. Its alcoholic solution gives with lead acetate a precipitate containing $C^{26}H^{44}O^{5}.PbO$.

BRAZILIN, the colouring matter of Brazil wood, discovered by Chevreul, has been shown by Bolley to be identical with that of sapan wood (v. 191). The statements respecting this colouring matter given in vol. i. p. 655, on the authority of Preisser, are not to be trusted.

BROCHANTITE. Native tetracupric sulphate. $CuSO^{4}.3CuH^{2}O^{2}$. See SULPHATES.

BROMINE. According to J. Slessor (*New Edinb. Phil. J.* vii. 287), aqueous solutions of bromine of different densities contain the following quantities by weight of bromine in 1,000 parts of water:

Density	Br. per 1,000	Density	Br. per 1,000
1·00901	10·72	1·01491	18·70 to 19·06
1·00931	10·78	1·01585	19·52 „ 20·09
1·00995	12·05	1·01807	20·89 „ 21·55
1·01223	12·3	1·02367	31·02 „ 31·69

At the density of 1·02367 bromine-water is saturated.

Dancer (*Chem. Soc. J.* xv. 477) has determined the solubility of bromine in water at different temperatures:

Temp.	Br. per cent.	Temp.	Br. per cent.
5°	3·600	20°	3·208
10°	3·327	25°	3·167
15°	3·226	30°	3·126

When a current of electricity is passed through bromine-water or aqueous hydrobromic acid, bromic acid is formed at the positive pole.

Bromine-vapour bleaches moist litmus-paper, but not permanently, the paper on exposure to the air turning red in consequence of the formation of hydrobromic acid: the original colour is restored by ammonia (Reinsch, *N. Jahresb. Pharm.* xi. 269).

Bromine in presence of water, and under the influence of direct sunshine, oxidises many neutral organic compounds and converts them into acids: such is the case with benzene, toluene, mannite, sugar, glycerin, &c. (Blomstrand, *Ann. Ch. Pharm.* cxxiii. 248).

Detection and Estimation of Bromine.—Fresenius (*Zeitschr. anal. Chem.* i. 46) recommends the use of chloroform or carbon bisulphide instead of ether in testing for bromine by means of chlorine. In a liquid containing only $\frac{1}{20.000}$ part of bromine, ether does not become coloured after addition of chlorine; but chloroform or carbon bisulphide under the same circumstances exhibits a pale yellow colour. A solution containing only $\frac{1}{30.000}$ of bromine colours carbon bisulphide, but not chloroform. If an iodide is also present, the violet coloration due to the iodine is first observed, and when this has been made to disappear by further addition of chlorine, the yellow tint of the bromine becomes apparent. Phipson (*ibid.* vii. 97) acidulates the dilute solution with hydrochloric acid, mixes it in a tube two feet long with a small quantity of carbon bisulphide, and agitates it with a strong solution of chloride of lime.

Reimann (*Ann. Ch. Pharm.* cxv. 140) estimates bromine, in presence of iodine and chlorine, by means of a graduated solution of chlorine. Thus, to analyse a mixture of bromide and iodide of potassium, a quantity of chloroform is first added, such that, after agitation, a drop about the size of a nut may remain undissolved, and the graduated chlorine-water is added by small portions. The chloroform then acquires a blue or rose colour, which disappears completely as soon as 6 atoms of chlorine have been added to 1 mol. of the iodide, the ultimate products of the reaction being potassium iodate and hydrochloric acid:

$$Cl^6 + KI + 3H^2O = KIO^3 + 6HCl.$$

On continuing the addition of the chlorine-water, the chloroform becomes first yellow, then orange-coloured, then again yellow, and finally, when 2 at. chlorine have been added to 1 at. bromine, yellowish-white:

$$KBr + Cl^2 = KCl + BrCl.$$

If organic substances are present, the liquid must be previously mixed with caustic soda, evaporated to dryness, and the residue ignited in a silver dish.

The following method, founded, like that of Field (i. 678), on the differences between the atomic weights of chlorine, bromine, and iodine, is given by R. Tatlock (*Chem. News*, 1869, p. 290). The solution containing the iodine, bromine, and chlorine, preferably in combination with an alkali-metal, is divided into three equal portions, one of which is treated with excess of silver nitrate to precipitate the whole of the iodine, bromine, and chlorine. The second is treated with excess of bromine-water to decompose the iodide, and then precipitated with silver nitrate, which throws down bromide and chloride of silver. The third portion is treated with excess of chlorine to decompose the iodide and bromide, and yields a precipitate consisting wholly of silver chloride. These three precipitates having been weighed, the quantities of iodine, bromine, and chlorine may be calculated by the method given in vol. i. p. 679.

To apply this method to the analysis of kelp, the kelp is digested in hot water; the filtrate and washings are neutralised with hydrochloric acid; chlorine is passed into the solution; and the liquid is shaken up with about one-fourth its volume of carbon bisulphide to dissolve the liberated iodine and bromine. The heavy, coloured solution of these elements is then drawn off by a fine syphon, and shaken up with water and zinc-filings, whereby a solution of zinc bromide and iodide is obtained, in which the iodine and bromine may be estimated as above.

For the estimation of bromine in organic compounds, see ANALYSIS, ORGANIC (p. 148).

Bromides. *Hydrogen Bromide* or *Hydrobromic Acid* is produced directly by subjecting a mixture of dry bromine-vapour and hydrogen gas to the prolonged action of the induction-spark (A. Riche, *Compt. rend.* xlvi. 348).

Kekulé (*Ann. Ch. Pharm.* cxxx. 14) prepares pure aqueous hydrobromic acid by passing the gas evolved by allowing a slow stream of water to flow upon phosphorous tribromide, into water or dilute hydrobromic acid, till a saturated solution is formed; heating this solution (which still contains a considerable quantity of phosphorous bromide); and passing the gas thereby evolved either into pure water or into pure dilute hydrobromic acid.

Metallic Bromides.—According to Henner a. Hohenhauser (*Jahresb.* 1864, p. 148), the process recommended by Klein for the preparation of metallic bromides (see Potassium Bromide, iv. 696) is not adapted for production on the large scale. These chemists dissolve bromine in a slight excess of barium or calcium hydrate; evaporate the clear liquid to the crystallising point; precipitate the bromates (to be reduced to bromides by ignition with charcoal) with alcohol of 90 p. c., then distil off the alcohol, and evaporate the remaining liquid to the crystallising point.

Potassium bromide is most easily prepared from the barium salt by precipitation with potassium sulphate.

Chloride of Bromine. When a light yellow mixture of equal volumes of saturated chlorine-water and of bromine-water containing 1 p. c. bromine, is treated with oxidisable substances, it first assumes a brown-red colour, and then, on further addition of the oxidisable substance, becomes perfectly colourless. This reaction is produced by finely divided sulphur or phosphorus, zinc or iron filings, ferrous or stannous salts, nitrogen dioxide and tetroxide, sulphurous, hypophosphorous, phosphorous, arsenious, oxalic, and formic acids, hydrogen dioxide, and ammonia. The chlorine, under these circumstances, is converted into hydrochloric acid, and if the quantity of the reducing agent is sufficient, the bromine is likewise converted into hydrobromic acid. Oxalic acid alone exhibits an exception to this general rule, being oxidised by chlorine, but not by bromine, and therefore colouring the liquid brown, even when in considerable excess. Hydrogen dioxide is resolved into oxygen and hydrogen, which latter unites with the chlorine and bromine. Ether shaken up with the yellow solution takes up the bromine chloride, forming a solution which exhibits the reactions above described. These reactions show that bromine may be detected in presence of free chlorine by the cautious addition of reducing agents (Schönbein, *Ann. Ch. Pharm. Suppl.* ii. 211).

Oxygen-acids of Bromine.

Bromic Acid. $HBrO^3$.—According to Kämmerer (*J. pr. Chem.* lxxxv. 452), this acid, prepared by the usual method of decomposing a metallic bromate with an acid, is not pure, because the decomposition of bromates by the stronger acids is never complete. It may, however, be obtained absolutely pure by the direct action of chlorine on aqueous bromine, or by decomposing silver bromate with bromine:

$$5AgBrO^3 + 3Br^2 + 3H^2O = 5AgBr + 6HBrO^3.$$

Kämmerer obtained a hydrated bromic acid containing $HBrO^3.7H^2O$, and is of opinion that another hydrate, $2HBrO^3.9H^2O$, exists at very low temperatures.

The bromates of the *alkali-metals* are advantageously prepared by passing bromine into solutions of alkaline carbonates, previously saturated with chlorine till they begin to effervesce; the ultimate products of the reaction are chlorine gas, which escapes, and nearly pure bromate of the alkali-metal. From either of these salts the bromate of silver may be obtained by double decomposition.

Didymium bromate, $Di(BrO^3)^2.6H^2O$, crystallises in rose-red hexagonal prisms $\infty P : P$, permanent in the air, seldom distinctly developed at the ends. Angle $P : P$ in the terminal edges = 147° 58′, in the lateral edges = 67°. Cleavage distinct parallel to oP. *Lanthanum bromate* forms crystals of similar character (Marignac, *Ann. Min.* [5] xv. 272).

Perbromic acid, $HBrO^4$, is produced by the action of bromine on perchloric acid (iv. 374).

Hypobromous acid, $HBrO$, is formed by the action of bromine and water on silver nitrate and on mercuric oxide (iii. 237); also, according to Schönbein (*Jahresb.* 1862, p. 66), on mercuric chloride, nitrate, or acetate.

BROMOFORM. $CHBr^3$.—Produced from dibromosuccinic acid by the action of bromine in excess in presence of water (Kekulé, *Ann. Ch. Pharm. Suppl.* i. 354):

$$C^4H^4Br^2O^4 + 2H^2O + 4Br^2 = CHBr^3 + 3CO^2 + 7HBr.$$

Decomposed by ammonia, with formation of bromide and cyanide of ammonium (Cloez, *Compt. rend.* xlvi. 344):

$$CHBr^3 + 5NH^3 = 3NH^4Br + NH^4CN.$$

It acts strongly on zinc-ethyl, producing ethyl bromide, zinc bromide, and propylene (Alexeyeff a. Beilstein, *Bull. Soc. Chim.* [2] ii. 51):

$$CHBr^3 + (C^2H^5)^2Zn = C^2H^5Br + ZnBr^2 + C^3H^6.$$

BROMOXAFORM, $C^3HBr^5O^2$, originally obtained by Cahours by the action of bromine on solution of potassium citrate (i. 996), is likewise formed, under certain circumstances, by the action of an excess of bromine on dibromocitraconic acid:

$$C^5H^4Br^2O^4 + 2H^2O + 6Br^2 = 2CO^2 + 9HBr + C^3HBr^5O^2.$$

It is separated from the distillate by water as a heavy oil which soon solidifies. It melts at 77°, dissolves easily in alcohol and ether, and crystallises from the former in long hard needles, from the latter in thick transparent prisms. By distillation with potash, it yields bromoform; with alcoholic ammonia, dibromacetamide (Cahours, *Ann. Ch. Phys.* [3] lxvii. 129; *Jahresb.* 1862, p. 318).

BRUCINE. $C^{23}H^{26}N^2O^4$.—According to Wittstein (*Arch. Pharm.* [2] c. 129; cix. 28), this alkaloïd exists, together with strychnine, in the urari or curara poison (ii. 185); but according to Buchner (*ibid.* cx. 19), this poison contains curarine, but neither strychnine nor brucine.

Brucine heated in a small cup of platinum-foil covered with a watchglass (p. 87) yields a granular sublimate which becomes crystalline by contact with sulphuric or nitric acid, and is converted by ammonia into a deep yellow amorphous mass, and by chromic acid into dark yellow stars or rosettes formed of short prisms (Helwig, *Zeitschr. anal. Chem.* iii. 43). With *phosphomolybdic acid*, brucine forms an orange precipitate, which dissolves in ammonia with yellow-green colour, turning brown on boiling (Trapp, *Jahresb.* 1863, p. 702). According to F. F. Mayer (*Rép. Chim. app.* v. 102), a solution of brucine containing 1 pt. in 50,000 produces a perceptible precipitate with a solution of *potassio-mercuric iodide* formed by dissolving 13,546 grms. mercuric chloride ($\frac{1}{10}$ eq.) and 49·8 grms. potassium iodide in a litre of water. This reaction may be used for the quantitative estimation of brucine (iii. 1053).

When a strong solution of *sodium sulphydrate* is added to a solution of brucine in nitric acid heated to 40°–50°, the liquid assumes at first a violet colour, and after the sodium salt has been added in excess, a fine green colour, which is not altered by alkalis, but is changed by dilute acids into rose-red, with evolution of hydrogen sulphide. After a day or two the green colour disappears, and a greenish precipitate appears. This mode of testing, if well performed, will reveal the presence of 0·002 grm. brucine in half a litre of water (S. Cotton, *Zeitschr. f. Chem.* [2] v. 728).

Brucine treated with a chlorate or with chlorine tetroxide in presence of strong sulphuric acid, assumes an orange-red colour, which does not turn violet on addition of stannous chloride. Free chloric and perchloric acids do not exhibit this reaction (Luck, *ibid.* vi. 275).

Methyl-brucine. $C^{23}H^{25}(CH^3)N^2O^4$.—Brucine is converted by methyl iodide, with evolution of heat, into *methyl-brucine hydriodide*, $C^{23}H^{25}(CH^3)N^2O^4.HI$, or *methyl-brucium iodide*, $C^{23}H^{26}(CH^3)N^2O^4.I$, which crystallises from boiling water in shining laminæ containing 8 mol. water of crystallisation. It is not further altered by repeated treatment with methyl iodide. By decomposing this salt with recently precipitated silver iodide (or the sulphate with baryta-water) a solution of the free base is obtained, which is colourless at first, but soon turns violet, and when evaporated gives off carbon dioxide and leaves a dark-coloured uncrystallisable syrup, apparently containing a base different from methyl-brucine. The *hydrobromide of methyl-brucine*, $C^{24}H^{28}N^2O^4.HBr + \frac{5}{2}aq.$, is formed on mixing the hydrochloride with potassium bromide, as a crystalline precipitate which dissolves easily in alcohol and water, and crystallises from the latter in small shining prisms, which give off their water at 130°. The *hydrochloride*, $C^{24}H^{28}N^2O^4.HCl + 5aq.$, obtained by neutralising the free base with hydrochloric acid, forms small shining crystals, easily soluble in water and in alcohol. The *platinochloride*, $2(C^{24}H^{28}N^2O^4.HCl).PtCl^4$, is a yellow precipitate, insoluble in ether, easily soluble in alcohol and in water, and crystallises from the latter in needles. The *aurochloride*, $C^{24}H^{28}N^2O^4.HCl.AuCl^3$, is an orange-yellow precipitate slightly soluble in cold water. Mercuric chloride added to the solution of the hydrochloride forms a white precipitate. The *neutral sulphate*, $(C^{24}H^{28}N^2O^4)^2.H^2SO^4 + 8aq.$, obtained by decomposing the hydriodide with silver sulphate, forms a radiate crystalline mass easily soluble in water and in alcohol. An *acid sulphate*, $C^{24}H^{28}N^2O^4.H^2SO^4 + 2aq.$, obtained from the preceding by addition of dilute sulphuric acid, forms indistinct crystals, somewhat easily soluble in water and in alcohol. Methyl-brucine given in the form of sulphate to rabbits in doses of ten grains exerts no poisonous action (Stahlschmidt, *Pogg. Ann.* cviii. 513; *Jahresb.* 1859, p. 398).

The experiments of Crum-Brown a. Fraser (*Edin. Phil. Trans.* vol. xxv.) have also shown that the salts of methyl-brucine are much less poisonous than those of brucine; moreover, their physiological action is different from that of brucine: the latter is a violent convulsive poison, whereas its methyl-derivatives, though fatal in large doses, never produce convulsions.

Ethyl-brucine, $C^{23}H^{25}(C^2H^5)N^2O^4$, is described in vol. i. p. 684.

Brucine-bromethylammonium. $C^{25}H^{30}N^2Br^2O^4$.—Brucine unites directly with ethylene bromide when the two are heated together to 100°, forming a clear liquid, which on cooling solidifies to a crystalline mass, and when recrystallised from boiling water forms furcate groups of nacreous laminæ, easily soluble in water, sparingly soluble in alcohol, insoluble in ether. This compound, which contains the elements of brucine and ethylene bromide, may be regarded as *Brucine-bromethylammonium bromide*, $\left.\begin{matrix}C^{23}H^{26}N^2O^4\\ C^2H^4Br\end{matrix}\right\}Br$, the brucine exhibiting the functions of a tertiary amine. The crystals when air-dried contain 3 molecules of water. The solution of this bromide is not precipitated by ammonia or the fixed alkalis. Silver nitrate throws down half, and recently precipitated silver oxide at the boiling heat the whole of the bromine as silver bromide. The corresponding *platinochloride*, $2(C^{23}H^{26}N^2O^4.C^2H^4BrCl).PtCl^4$, is an orange-yellow crystalline precipitate.

Brucine-vinylammonium hydrate, $C^{23}H^{26}N^2O^4.C^2H^3(OH)$, is the base formed by treating the aqueous solution of the above-described bromide with moist silver oxide. The resulting solution has a strong alkaline reaction, absorbs carbonic acid from the air, and dries up to a brown varnish exhibiting traces of crystallisation. Its *platinum salt* has the composition $2(C^{23}H^{26}N^2O^4.C^2H^3Cl).PtCl^4$. An *acid sulphate*, forming hydrated crystals, is obtained by treating the base with excess of dilute sulphuric acid (L. Schad, *Ann. Ch. Pharm.* cxviii. 207).

Periodides of Brucine (S. M. Jörgensen, *Ann. Ch. Phys.* [4] xi. 114).—*Brucine Hydro-triiodide*, $C^{23}H^{26}N^2O^4.HI^3$, or *Brucium Tri-iodide*, $C^{23}H^{27}N^2O^4.I^3$, is obtained, by mixing brucine sulphate with a solution of iodine in potassium iodide, as a brown-red precipitate crystallising from alcohol in long brown-violet needles, which in polarised light appear light yellow when their longitudinal axis is parallel to the plane of polarisation, and purple-brown with blue shade when the same axis is at right angles to the plane of polarisation.

Brucine Methyl-triiodide, $C^{23}H^{26}N^2O^4.CH^3I^3$, or *Methyl-brucium Tri-iodide*, $C^{23}H^{26}(CH^3)N^2O^4.I^3$, crystallises from a mixture of 1 mol. methyl-brucium iodide and 2 at. iodine, in rosettes of brown-red laminæ, which are yellowish-red by transmitted, dark blue by reflected light, and have no action on polarised light. *Methyl-brucium Penta-iodide*, $C^{23}H^{26}(CH^3)N^2O^4.I^5$, separates from the solution of the last-described compound in tincture of iodine, in nearly black prisms, which are blue by reflected light, and in polarised light appear opaque and black, or more or less dark red, accordingly as their longitudinal axis is parallel or perpendicular to the plane of polarisation.

Ethyl-brucium Tri-iodide, $C^{23}H^{26}(C^2H^5)N^2O^4.I^3$, obtained like the methyl-compound, separates from alcohol in hemispherical groups of reddish-yellow crystals having a golden lustre, and exhibiting in mass the aspect of reduced copper. The *penta-iodide*, $C^{23}H^{26}(C^2H^5)N^2O^4.I^5$, crystallises in four-sided needles, which in ordinary light have a deep metallic green colour, and in polarised light appear opaque or a purple-red, accordingly as their longitudinal axis is parallel or perpendicular to the plane of polarisation.

Amyl-brucium Tri-iodide, $C^{23}H^{26}(C^5H^{11})N^2O^4.I^3$, crystallises in very thin yellowish-red needles which have a silky lustre, and in polarised light appear brown or yellow accordingly as their axis is parallel or perpendicular to the plane of polarisation. The *penta-iodide*, $C^{23}H^{26}(C^5H^{11})N^2O^4.I^5$, crystallises in long bluish-green, metallically lustrous rhombic needles, which, on account of their perfect opacity, cannot be examined in polarised light.

Allyl-brucium Tri-iodide, $C^{23}H^{26}(C^3H^5)N^2O^4.I^3$, obtained like the methyl-compound, forms stellate groups of brown crystals, which in polarised light are yellow or red according to their position. The *penta-iodide*, $C^{23}H^{26}(C^3H^5)N^2O^4.I^5$, crystallises in splendid long four-sided needles having the colour and lustre of the wing-cases of cantharides. The crystals are mostly opaque; the thinner ones appear in polarised light, deep violet-red or opaque, accordingly as their axis is parallel or perpendicular to the plane of polarisation.

BRUCITE. MgH^2O^2.—On the crystalline form of this mineral, see G. Rose (*Jahresb.* 1860, p. 753), Hessenberg (*ibid.* 1861, p. 989), and Brush (*ibid.* 1861, p. 990).

BRUSHITE. A dicalcic orthophosphate, $Ca^2H^2(PO^4)^2.4H^2O$, occurring in small crystals in guano from the island of Avis in the Caribbean sea; also together with other calcic phosphates in the guano of Sombrero. (See PHOSPHATES in this volume.)

BUCKWHEAT. *Polygonum fagopyrum.*—According to Nobbe a. Siegert (*Chem. Centr.* 1863, p. 296), whose results are corroborated by Leydhecker (*Jahresb.* 1867, p. 760), this plant forms ripe and germinating seeds only in soils containing potassium chloride or calcium chloride. In soils free from chlorine (containing only nitrates, sulphates, and phosphates) it grows, flowers, and begins to form fruit, but does not ripen its seeds. Even sodium or magnesium chloride cannot replace the chlorides of potassium and calcium.

J. W. Gunning (*Zeitschr. f. Chem.* [2] iv. 371) has analysed buckwheat flour with the following results:

	Friesland	French	Holstein
Water	15·39	15·29	15·17
Ash	1·08	0·94	0·82
Fat	1·98	1·96	1·63
Albuminous principles .	9·96	9·16	8·63
Starch	59·84	61·35	62·62
Cellulose . . .	11·75	11·29	8·63

The yellow colouring matter of buckwheat (i. 686) has been further examined by Schunck (*Manchester Lit. and Phil. Soc. Memoirs*, 1858; *Jahresb.* 1859, p. 527), who assigns to it the formula $C^{15}H^{20}O^{10}$, and to its lead-salt the formula $C^{15}H^{18}PbO^{10}$. Schunck regards this colouring matter as identical with rutin and ilixanthin, though the preceding formula does not quite agree with the formulæ attributed to these compounds (iii. 244; v. 139).

BUCKLANDITE. (See EPIDOTE).—The mineral of this name from Laach in the Eifel has been shown by v. Roth to be identical with orthite (iv. 238).

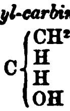
BUTALANINE. Syn. with AMIDOVALERIC ACID. (See VALERIC ACID, v. 978).

BUTAMYLENE. See AMYLENE.

BUTYL ALCOHOLS. These compounds have been described in vol. v. 732, under the title TETRYL ALCOHOLS. Recent researches, however, have somewhat modified the account to be given of them.

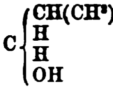
The butyl alcohol of fermentation is a *primary* alcohol, not the *normal primary*, as was believed until quite recently, but the abnormal or iso-primary. There are two varieties of primary butylic alcohol, viz. *Propyl-carbinol*, and *Isopropyl-carbinol*.

Propyl-carbinol or *Normal Primary Butylic alcohol*,



$$C\begin{cases}CH^2CH^2CH^3\\H\\H\\OH\end{cases}$$

is comparatively little known, and has not hitherto been found as a natural product. It was obtained synthetically by Schöyen (*Ann. Ch. Pharm.* cxxx. 235) from ethyl gas, by submitting it to the action of chlorine and subsequent conversion of the resulting butyl chloride into butyl acetate, which latter product was transformed into the alcohol. A much more complete investigation of this compound has been just published by Lieben and Rossi (*Compt. rend.* lxviii. [1869] 1561 *et seq.*). These chemists first prepared butyric aldehyde by distilling a mixture of butyrate and formate of calcium. From the aldehyde the alcohol was obtained by hydrogenation with sodium-amalgam. The alcohol, when perfectly dried, boils at 115°. It is considerably lighter than water. In smell it resembles isobutylic alcohol. It is very sparingly soluble in water. Treated with sodium, it gives sodium butylate, with disengagement of hydrogen gas. Iodine and phosphorus transform it into the iodide, boiling at 127°. Oxidation by means of dilute chromic acid gives normal butyric acid, unaccompanied by any other acid.

Isopropyl-carbinol or *Isoprimary-butylic Alcohol.* 
$C\begin{cases}CH(CH^3)^2\\H\\H\\OH\end{cases}$
—This alcohol constitutes the butylic alcohol of Wurtz, which was extracted from fusel-oil. For a long time it was the only butyl alcohol known to chemists. Erlenmeyer and also Chapman have recently shown that this common butylic alcohol gives isobutyric acid, by oxidation with dilute chromic acid, and that therefore it is an iso-alcohol. On its occurrence in crude spirit, see Krämer a. Pinner (*Zeitschr. f. Chem.* [2] v. 690). It has recently been examined very completely by Chapman a. Smith (*Chem. Soc. J.* 1869 [2] vii. 153). Its boiling point is 109°, being sensibly lower than that of the normal alcohol. Sp. gr. = 0·8055 at 16·8°. It dissolves 1 at. sodium but slowly, and only on brisk agitation and warming; but calcium chloride, potassium acetate, and potassium hydrate are dissolved by it with facility. It mixes easily with glacial acetic acid, with the same acid diluted with twice its bulk of water, and with hydrochloric acid. It dissolves in about eleven times its own bulk of water. By strong sulphuric acid at −15° to −16° it appears to be completely converted into butyl-sulphuric acid; at ordinary temperatures chiefly into polymerides of butylene; with sulphuric acid diluted with three times its weight of water, it yields chiefly butyl-sulphuric acid. The dilute and gently warmed solution of this acid deposits, on addition of an excess of crystallised Glauber's salt, a colourless peculiar-smelling liquid which appears to be a hydrate of isobutyl alcohol, inasmuch as it is resolved by distillation into water and that alcohol.

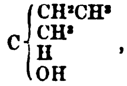
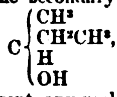
Respecting the conversion of isobutyl alcohol into tertiary butyl alcohol, see p. 374.

The various compounds described in vol. v. as derivatives of normal butyl alcohol are in reality derivatives of isopropyl-carbinol. According to Chapman a. Smith, the iodide and bromide cannot be advantageously prepared by the action of iodine or bromine and phosphorus on isobutyl alcohol, since in both cases a large quantity of the alcohol is converted into butylene.

The *bromide*, C^4H^9Br, is best prepared by saturating the alcohol with gaseous hydrobromic acid, and then heating it to 100° in sealed tubes with an equal volume of aqueous hydrobromic acid of sp. gr. 1·6, till the separated oily layer no longer increases. On fractional distillation the greater part goes over at 92°, but a small portion having the same composition distils 16° or 17° lower. The colourless bromide boiling at 92° has a sp. gr. of 1·2702 at 16°, and behaves with reagents just like the iodide.

Isobutyl iodide, C^4H^9I, is most easily prepared by boiling the alcohol for thirty or forty minutes with four times it volume of hydriodic acid of sp. gr. 1·8. The greater part of the product distils constantly at 121°. Sp. gr. = 1·6301 at 0°; 1·6032 at 16°; 1·54816 at 50°. By alcoholic potash or sodium ethylate it is for the most part converted into butylene, only a small portion yielding butyl-ethyl oxide. Alcoholic ammonia converts it into butylamine, with little or no butylene. Heated with potassium acetate and glacial acetic acid, it is chiefly converted into isobutyl acetate, a small quantity of butylene being however formed at the same time. Heated with mercuric chloride it yields butyl chloride and a small quantity of butylene. Heated with zinc and ether, it gives off a large quantity of gas, and yields but little zinc-butyl. With sodium-amalgam and ethyl acetate it yields mercury-butyl, together with a large quantity of gas. Potassium cyanide converts it into butyl-cyanide without much formation of butylene. With sodium it gives off butylene and butyl-hydride, with but little butyl.

Morkownikoff has lately shown that this iodide may be converted into tertiary butyl iodide, $(CH^3)^3CI$, by heating it with alcoholic potash, which abstracts HI and leaves isobutylene, and then combining the latter directly with HI (p. 374).

Secondary Butylic Alcohol. The possible forms of the secondary alcohol are *ethyl-methyl carbinol*, 
$C\begin{cases}CH^2CH^3\\CH^3\\H\\OH\end{cases}$
, and *methyl-ethyl carbinol*, 
$C\begin{cases}CH^3\\CH^2CH^3\\H\\OH\end{cases}$
, but according to our present theory these two formulæ do not represent any real difference of composition, and there is consequently only one secondary butylic alcohol, which may bear either of the above names.

De Luynes obtained the secondary alcohol from erythrite by reduction with hydriodic acid. Lieben has also obtained it by another process, viz. by the successive action of zinc-ethyl and hydriodic acid on chlorinated ether (*Ann. Ch. Pharm.* cxli. 236).

The changes which take place in the latter process are expressed by the following equations:

$$(1)\quad \left.\begin{matrix}C^2H^3Cl^2\\C^2H^5\end{matrix}\right\}O + Zn(C^2H^5)^2 = Zn\left\{\begin{matrix}C^2H^5\\Cl\end{matrix}\right. + \left.\begin{matrix}C^2H^3C^2H^5Cl\\C^2H^5\end{matrix}\right\}O$$

$$(2)\quad \left.\begin{matrix}C^2H^3C^2H^5Cl\\C^2H^5\end{matrix}\right\}O + 4HI = \left.\begin{matrix}C^2H^3C^2H^5H\\I\end{matrix}\right\} + HCl + H^2O + C^2H^5I + I^2.$$

The resulting organic iodide, $C^2H^3C^2H^5HI$, may then be either at once treated with moist silver oxide, or else converted into acetate, which latter is transformable, in the usual manner, into the alcohol. This alcohol boils at 99°, according to Lieben and Bauer. According to De Luynes, the boiling point is 95° to 98°. Its sp. gr. at 0° is 0·827 (Lieben a. Bauer); 0·850 (De Luynes). By oxidation it yields neither normal nor isobutyric acid, but acetic acid. See further v. 734, where this alcohol is described as isotetrylic alcohol.

Secondary butyl iodide, $C\left\{\begin{matrix}C^2H^5\\CH^3\\H\\I\end{matrix}\right.$, is described at p. 736, vol. v., as isotetrylic iodide.

Tertiary Butyl Alcohol. Trimethyl-carbinol. $C\left\{\begin{matrix}CH^3\\CH^3\\CH^3\\OH\end{matrix}\right.$.—Discovered by Buttlerow (*Ann. Ch. Pharm.* cxliv. 1). At the ordinary temperature of the air it is a solid substance. Buttlerow prepared it by the slow action of excess of zinc-methyl on acetyl chloride. 100 grms. of acetyl chloride were slowly dropped into 250 grms. of zinc-methyl, the latter being kept cool by immersion of the containing vessel in cold water. After the lapse of several days, water was added to the product, until it ceased to give a precipitate. A certain quantity of oily product separated on this treatment, and this was carefully removed from the aqueous liquid, which contained the trimethyl-carbinol in solution. Carbonate of potassium was next added to the aqueous solution, whereupon the new alcohol formed an oily layer which was subsequently dried (when it solidified). From the above quantity of materials 75 grms. of trimethyl-carbinol were obtained. The boiling point is 82°. It forms large colourless crystals.

The reaction by which the tertiary alcohol is produced is the following:

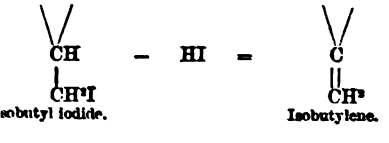
$$CO\left\{\begin{matrix}CH^3\\Cl\end{matrix}\right. + 2Zn\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right. = C\left\{\begin{matrix}CH^3\\CH^3\\CH^3\\OZnCH^3\end{matrix}\right. + Zn\left\{\begin{matrix}CH^3\\Cl\end{matrix}\right..$$

On adding the water there is disengagement of gaseous methyl hydride and formation of zinc hydrate and the tertiary alcohol.

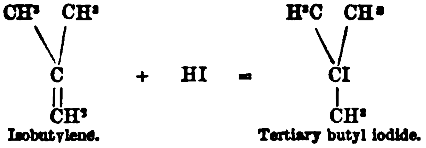
This alcohol may also be formed from the primary alcohol of fermentation (*vide infra*).
J. A. W.

Tertiary Butyl Iodide or *Trimethyl Carbonyl Iodide*, $C(CH^3)^3I$, is easily formed by passing gaseous hydriodic acid into well-cooled trimethyl-carbinol, or, though less completely, by agitating the alcohol with fuming hydriodic acid. The iodide decolorised by caustic potash or alkaline bisulphite, and dried over calcium chloride, is a heavy liquid, insoluble in water, smelling like petroleum, and boiling, with partial decomposition, at 98°–99°. With a solution of potash in strong alcohol, it is easily resolved into butylene and hydriodic acid; if, however, water is present, a large quantity of trimethyl-carbinol is formed, with but little butylene. By dry silver-oxide it is decomposed explosively; with moist silver oxide it yields trimethyl-carbinol and a small quantity of butylene.

This iodide has lately been obtained in a remarkable manner by Morkownikoff (*Zeitschr. f. Chem.* [2] vi. 29), from isobutyl-iodide or isopropyl-carbinyl iodide, by heating the latter with alcoholic potash, whereby it is converted into isobutylene, and combining the latter directly with hydriodic acid. The conversion is represented by the following equations:



Isobutyl iodide. Isobutylene.

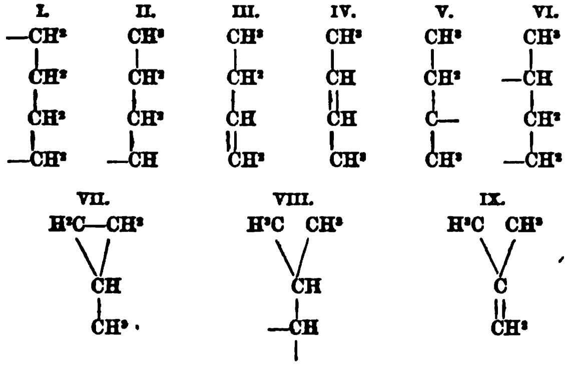


The tertiary butyl iodide thus obtained is converted by moist silver oxide into tertiary butyl alcohol, identical with that obtained by Buttlerow (see also Buttlerow, *ibid.* vi. 237).

Tertiary Butyl Chloride, $C(CH^3)^3Cl$, is formed, together with the corresponding acetate, by the action of acetyl chloride on trimethyl-carbinol; also by the action of phosphorus pentachloride on that alcohol. By prolonged heating to 100° with water it is resolved into hydrochloric acid and trimethyl-carbinol. Buttlerow has observed the formation of trimethyl-carbinol by the action of water on a butyl chloride prepared from commercial alcohol: hence it appears probable that this tertiary alcohol likewise occurs amongst the products of alcoholic fermentation.

Tertiary Butyl Acetate, $C^6H^{12}O^2 = C(CH^3)^3.C^2H^3O^2$, is easily obtained by mixing the iodide with silver acetate previously moistened with strong acetic acid. After rectification over silver acetate, washing with water, and drying over calcium chloride, it forms an aromatic oil, smelling like mint and acetic acid, soluble in a large quantity of water, boiling at 96°, and resolved by heating with baryta-water into barium acetate and trimethyl-carbinol.

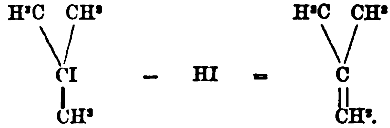
BUTYLENE. C^4H^8.—This hydrocarbon might exhibit the following modifications:



The modifications I. to V. might be formed by dehydration of normal butyl alcohol or propyl-carbinol; II. to V., also from secondary butyl-alcohol or methyl-ethyl carbinol; VI., only from the latter; VII., VIII., and IX., from isopropyl carbinol; VII. and IX., also from the tertiary alcohol (trimethyl-carbinol).

Our actual knowledge of these modifications is, however, very incomplete. *a.* The hydrocarbons C^4H^8 described under TETRYLENE (v. 737)—as produced by the condensation of oil-gas, by the electrolysis of valeric acid, by the dehydration of isobutyl carbinol with sulphuric acid, and by the action of alcoholic potash on secondary butyl iodide—are probably not all identical. That obtained by the first process boils below 0° (Faraday); that obtained from secondary butyl iodide at + 3° (De Luynes). The latter may have the constitution represented by either of the formulæ III., IV., V., or VII., according to the particular hydrogen-atom which is removed from the molecule $\left\{\begin{array}{l}CH^3\\CH^2\\CHI\\CH^3\end{array}\right.$, in combination with the iodine. Lieben (*Ann. Ch. Pharm.* cli. 121) by combining this butylene (boiling at + 1°) with hypochlorous acid, and treating the resulting chlorhydrin, $C^4H^8\left\{\begin{array}{l}Cl\\OH\end{array}\right.$, with sodium-amalgam, has obtained secondary butyl alcohol, whence he infers that the butylene in question has the constitution IV. or V.

β. *Dimethyl-ethylene*, $C^2H^2(CH^3)^2$, Buttlerow's *pseudobutylene*, as obtained by heating tertiary butyl-iodide with alcoholic potash, has the composition represented by formula IX.:



It is given off as a gas, which may be freed from condensable products by passing through a bottle and bulb-apparatus cooled by water. It smells like coal-gas, burns with a very bright but sooty flame, is quickly absorbed by strong sulphuric or hydriodic acid, and condenses at 15°–18° under a pressure of 2 to 2½ atmospheres to a liquid which boils at −7° to −8° under a pressure of 752 millim. By its combination with hydriodic acid, tertiary butyl iodide is reproduced, whereas butylene from erythrite yields secondary butyl iodide (v. 736). Strong sulphuric acid absorbs dimethyl-ethylene, with separation of a liquid capable of combining with bromine, and apparently consisting of polymerides of butylene. A mixture of 2 vol. strong sulphuric acid and 1 vol. water absorbs the gas, with formation of trimethyl-carbinol, which may be separated by distillation from the solution after dilution with water.

Dimethyl-ethylene is likewise evolved on heating a solution of trimethyl-carbinol in sulphuric acid diluted with 2 vols. water; by heating isobutyl iodide with alcoholic potash; and by the electrolysis of ordinary valerianic acid.

Dimethyl-ethylene is absorbed by a cold solution of hypochlorous acid (obtained by passing chlorine into recently precipitated mercuric oxide mixed with ice); and the solution freed from excess of hypochlorous acid by means of sodium bisulphite yields by distillation, agitation of the distillate with ether, and evaporation of the latter, a liquid consisting of isobutylic chlorhydrin, $C\left\{\begin{array}{l}CCl(CH^3)^2\\H^2\\OH\end{array}\right.$, which has a burning taste, boils at 137°, and is converted by sodium-amalgam into isobutyl alcohol, $C\left\{\begin{array}{l}CH(CH^3)^2\\H^2\\OH\end{array}\right.$ (Buttlerow, *Ann. Ch. Pharm.* cxliv. 1; *Jahresb.* 1867, p. 578; further, *Zeitschr. f. Chem.* [2] vi. 236, 238).

γ. *Methyl-allyl.* $CH^3.C^3H^5$.—This modification of the hydrocarbon C^4H^8 may be structurally represented by the formula IV. or VII. It is produced by the action of zinc-methyl on allyl iodide:

$$Zn'CH^3 + C^3H^5I = Zn'I + CH^3.C^3H^5,$$

or more easily by heating a mixture of methyl-iodide and allyl-iodide (diluted with 2 vol. ether) with sodium to 100°:

$$CH^3I + C^3H^5I + Na^2 = 2NaI + CH^3.C^3H^5.$$

After several hours' action, the tubes are cooled, quickly connected with a receiver cooled to −12°, and then gently warmed. The ethereal liquid which passes over is saturated at a low temperature with bromine, and the brominated product, freed from excess of bromine by agitation with potash, and from ether by evaporation, is distilled under reduced pressure. If the distillation be interrupted when the thermometer shows a temperature of 100° under a pressure of 10 centim. of mercury, the residue, which solidifies on cooling, consists of diallyl-tetrabromide, and the portion which passes over yields by fractional distillation, a colourless mobile liquid, boiling between 155° and 166°, and having the composition of butylene bromide, $C^4H^8Br^2$. This liquid attacks the eyes, boils at 156°–159° under a pressure of 755 millim. (normal butylene bromide boils at 158°), and has a sp. gr. of 1·8299 to 1·8119 at 0°. Sodium decomposes it somewhat rapidly, forming a dry white mass; and on opening the tubes, previously cooled to −12°, a gas escapes, which may be condensed by cold to a liquid boiling between −4° and +8°. This liquid (methyl-allyl) forms with hydriodic acid the compound $C^4H^8.HI$, which in sp. gr., 1·643, and boiling point, 116°–118°, agrees sensibly with butylene hydriodide or secondary butyl iodide (v. 736) (Wurtz, *Bull. Soc. Chim.* [2] viii. 265).

δ. *Ethyl-vinyl*, $C^2H^3.C^2H^5$, may have the structure represented by II., III., or V. It is formed by the action of zinc-ethyl on bromethylene:

$$C^2H^3Br + Zn'(C^2H^5) = Zn'Br + C^2H^3.C^2H^5.$$

This reaction was first observed by Chapman (*Chem. Soc. J.* [2] v. 28), and has been further studied by Wurtz (*Zeitschr. f. Chem.* [2] v. 407). The two bodies do not act on one another at ordinary temperatures, and the reaction takes place but slowly at 100°, or even at 140°; but when the heated tubes are left for several weeks, a white (or sometimes grey) crystalline precipitate of zinc bromide is formed. On opening the cooled tubes and passing the evolved gas into bromine, a bromide is formed which, after purification, is colourless, does not attack the eyes, has a sp. gr. of 1·876 at 0°, and boils at 165°–166° (bar. 755·5 mm.). On condensing the gas itself by a freezing mixture, liquid ethyl-vinyl was obtained, boiling between $-8°$ and 0°. The purer product obtained by decomposing the bromide in strong tubes with excess of sodium, and condensing the evolved gas in a freezing mixture, boiled constantly at $-5°$, gave with bromine a bromide $C^4H^8Br^2$, which boiled at 166°, was identical with that obtained directly as above, and when heated with concentrated hydriodic acid in a sealed tube to 100°, yielded an iodide, which, after purification, boiled at 120°–121°, and had a sp. gr. of 1·034 at 0°. This iodide is very much like ordinary butyl iodide, but is distinguished from that compound by the facility with which it acts on silver acetate at ordinary temperatures, yielding a butyl acetate which boils at about 110°, and gives with potassium hydrate a butyl alcohol boiling at about 95° (? secondary butyl alcohol).

The preceding characters are sufficient to show that ethyl-vinyl is different from ordinary butylene, pseudobutylene, and methyl-allyl.

BUTYRIC ACIDS. In the article ACIDS, ORGANIC (p. 40), it has been explained that butyric acid is the first of the series of fatty acids, $C^nH^{2n}O^2$, which admits of isomeric modifications, and that it exhibits the two modifications

$$C\left\{\begin{array}{l}CH^2CH^2CH^3\\O\\OH\end{array}\right. \qquad\qquad C\left\{\begin{array}{l}CH(CH^3)^2\\O\\OH\end{array}\right.$$

Normal Butyric acid. Isobutyric acid.

NORMAL BUTYRIC, PROPYL-FORMIC, OR ETHYL-ACETIC ACID is produced by oxidising propyl-carbinol, by decomposing normal propyl cyanide with acids or alkalis, and by the fermentation of sugar in contact with putrid curd. The same modification appears also to be formed in the putrefaction of diabetic urine (Klinger; Fonberg, *Jahresb.* 1858, p. 571), of wheat-flour (Sullivan, *ibid.* p. 231), and of rye-flour (Ritthausen, *Zeitschr. f. Chem.* [2] iv. 314); in the distillation of peat (*Jahresb.* 1858, p. 280; 1859, p. 742); in the oxidation of valeric acid by permanganic acid (Neubauer, *Ann. Ch. Pharm.* cvi. 59), and of Chinese wax by nitric acid (Buckton, *Chem. Soc. J.* x. 166); further by the following definite reactions:

α. By the action of hydriodic acid on succinic acid:

$$C^4H^6O^4 + H^6 = C^4H^8O^2 + 2H^2O$$

(Berthelot, *Bull. Soc. Chim.* ix. 455).—β. By fusing ethyl-crotonic acid with potash (Frankland a. Duppa, *Chem. Soc. J.* [2] iii. 133).

$$C^6H^{10}O^2 + 2KHO = C^4H^7KO^2 + C^2H^3KO^2 + H^2.$$

Ethyl-crotonic acid. Butyrate. Acetate.

γ. From filicic acid (dibutyryl-phloroglucin) by evaporation with potash-ley (Grabowsky, *Ann. Ch. Pharm.* cxliii. 279):

$$C^{14}H^{18}O^5 + 2H^2O = 2C^4H^8O^2 + C^6H^6O^3$$

Filicic acid. Butyric acid. Phloroglucin.

δ. In like manner from caïncetin and aphrodæscin (Rochleder, *Bull. Soc. Chim.* [2] ix. 382, 385):

$$C^{22}H^{34}O^3 + 3H^2O = 2C^4H^8O^2 + C^{14}H^{24}O^2$$

Caïncetin. Butyric acid. Caïncigenin.

$$C^{52}H^{82}O^{23} + 3H^2O = C^4H^8O^2 + 2C^{24}H^{40}O^{12}$$

Aphrodæscin. Butyric acid. Æscinic acid.

Butyric acid (probably normal) has been found ready-formed in flesh-juice, guano, excrements, putrid yeast, bad cider, and the water of peat-bogs, dung-heaps, and other accumulations of decomposing organic matter; also in the fruit of *Gingko biloba*, in œnanthic ether (wine fusel-oil) and in wood-tar (*Jahresb. f. Chem.* 1857, pp. 353, 402, 403, 559; 1859, pp. 363, 364; 1861, p. 454; 1866, p. 311).

It is only, however, within the last few years that normal butyric acid has been distinguished from its isomeride, and the accounts which have been given of the properties of butyric acid and butyric compounds generally must be taken to refer confusedly sometimes to one and sometimes to the other variety of the acid. In general, normal butyric derivatives have a slightly higher specific gravity and boiling point than the corresponding derivatives of isobutyric acid. Thus:

	Normal compounds.		Iso-compounds.	
Butyric Acids,	164°	0·9817 sp. gr.	154°	0·9598 sp. gr.
„ Anhydrides,	190°	—	180·5°	—
„ Chlorides,	—	—	92°	—
„ Ethyl-ethers,	119°	0·9019 sp. gr.	110°	0·8893 „

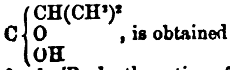
The specific gravities in the above tabular statement are given at 0° C. Normal butyric acid has a much more offensive smell than the iso-acid. There are also striking differences between the calcium salts of the two acids. Butyrate of calcium is more soluble in cold than in hot water, whereas the isobutyrate is more soluble in hot than in cold water.

Butyric acid heated with *bromine* in sealed tubes, is converted into mono- and dibromobutyric acids. With *chlorine* in sunshine, it yields di- and tetra-chlorobutyric acids (i. 694); in the shade it is very slowly attacked, apparently yielding monochlorobutyric acid; in presence of iodine this product is more quickly formed (Morkownikoff). With *sulphuric chlorhydrate*, it forms disulphopropiolic acid, $C^3H^6S^2O^6$, together with other products (Baumstark, *Ann. Ch. Pharm.* cxli. 25). By *permanganic acid* in alkaline solution, it is converted into succinic, propionic, acetic, and carbonic acids; and by hydriodic acid into butane or butyl hydride:

$$C^4H^8O^2 + 6HI = C^4H^{10} + 2H^2O + 3I^2$$

(Berthelot, *Jahresb.* 1867, pp. 335, 345).

ISOPROPYL-FORMIC ACID, DIMETHYL-ACETIC, or ISOBUTYRIC ACID,



$C\begin{cases} CH(CH^3)^2 \\ O \\ OH \end{cases}$, is obtained by oxidising isopropyl-carbinol (*i.e.* Wurtz's alcohol from fusel-oil); by the action of acids and alkalis on isopropyl cyanide; also by the oxidation of hexyl alcohol (Wanklyn a. Erlenmeyer), &c.

The existence of this acid, as distinguished from common butyric acid, was established in 1865 by Morkownikoff, who showed that the acid given by isopropyl cyanide (from glycerin) is distinct from the acid given by normal propyl cyanide. According to Morkownikoff, isobutyric acid (from isopropyl cyanide) boils at 153·5° to 154·5°. Sp. gr. 0·9598 at 0°; 0·9208 at 50°; 0·8965 at 100°. According to Chapman, isobutyric acid has not so high a degree of stability in presence of oxidising agents as the normal acid. J. A. W.

Isobutyrates.—The *potassium salt* remains on evaporation as a cauliflower-like deliquescent mass, easily soluble in alcohol. The *sodium salt* is crystalline. The *silver salt* $C^4H^7O^2Ag$ is a white precipitate, slightly soluble in cold water, and crystallising from a hot saturated solution in microscopic very flat rectangular plates; in a cold solution small prisms are also formed. The *barium salt* $(C^4H^7O^2)^2Ba$ is easily soluble in water and in alcohol, and difficult to crystallise; over sulphuric acid it crystallises in small prismatic forms; from a hot saturated solution, in efflorescent triclinic prisms. The *calcium salt* $(C^4H^7O^2)Ca . 5H^2O$ dissolves easily in hot water, and separates on cooling from a hot saturated solution, in a pulp of microscopic needles. From a not completely saturated solution it separates by slow cooling in long efflorescent prisms, and from a cold solution by slow crystallisation in four-sided monoclinic prisms $+P . -P . -(\infty P\infty) . \infty P\infty$, which are permanent in the air.

The *magnesium salt* $(C^4H^7O^2)^2Mg$ crystallises in white shining laminæ, easily soluble in water and in alcohol, and giving off part of their acid in drying. The *lead salt* crystallises from a solution of lead hydrate in the hot aqueous acid, in beautiful rhombic tables, which dissolve in 11 pts. water at 16°, and melt to a clear liquid in boiling water (normal lead butyrate prepared in the same manner separates from the cooling solution in oily drops, which unite into a viscid mass). The *cupric salt* is a blue-green precipitate slightly soluble in water, more soluble in alcohol, and crystallising in dark green prisms. *Mercury salts.*—A solution of recently precipitated mercuric oxide in the hot dilute acid deposits on evaporation a reddish-yellow crystalline mixture of mercuric and mercurous isobutyrate, and if afterwards left over sulphuric acid, yields spherical groups of needles, together with a pulverulent basic salt. In a solution of neutral mercurous nitrate, isobutyrates form a white crystalline precipitate, which blackens and partly dissolves at the boiling heat, and the solution deposits white interlaced needles, which in contact with water are converted, without change of form, into a yellow basic salt. *Ethyl isobutyrate*, $C^4H^7O^2.C^2H^5$, is a transparent colourless liquid, of purer and more agreeable odour than the butyrate, of sp. gr. 0·8893 at 0°, boiling at 110°, slightly soluble in water (Morkownikoff, *Ann. Ch. Pharm.* cxxxviii. 361).

Bromobutyric Acids (Friedel a. Machuca, *Ann. Ch. Pharm.* cxx. 279; *Suppl.* ii. 70. Gorup-Besanez a. Klinksieck, *ibid.* cxviii. 248. A. Naumann, *ibid.* cxix. 115. R. Schneider, *ibid.* 279).

Monobromobutyric acid, $C^4H^7BrO^2 = \left.\begin{matrix}C^4H^6BrO\\H\end{matrix}\right\}O$, may be prepared by heating 1 mol. butyric acid with 2 at. bromine to 130°–150° in sealed tubes for three or four hours. The tubes should be well cooled before they are opened; and the yellow liquid, consisting chiefly of bromobutyric acid, heated for a short time to 100°, and then treated with a small quantity of water, to remove the last traces of hydrobromic acid. The bromobutyric acid thus obtained contains about 20 p. c. water, which may be gradually removed by calcium chloride, the hydrate $C^4H^7BrO^2.H^2O$ being first produced, and afterwards the pure hydrogen bromobutyrate, $C^4H^7BrO^2$ (Schneider). According to Gorup-Besanez a. Klinksieck, the best way of obtaining the pure acid is to dissolve the contents of the tubes in four times their volume of alcohol; saturate the solution with hydrochloric acid gas; precipitate the resulting ethyl bromobutyrate with water; and, after purifying it in the usual way by washing, drying, and distillation, decompose it with recently precipitated lead hydrate, and separate the acid from the resulting lead salt by hydrogen sulphide.

Bromobutyric acid is an oily liquid, smelling of butyric acid and bromine, remaining liquid at −15°, having a sp. gr. of 1·54 at 15°, boiling at 180° (Schneider), at about 200° (Naumann), and then decomposing with rise of temperature. According to Friedel a. Machuca, it boils under ordinary pressure at 217° with partial decomposition, but under a reduced pressure of 3 mm. it boils without decomposition at 110°, and may thus be obtained colourless. Dissolves in 14 to 15 pts. water (Schneider); sparingly soluble in cold, moderately soluble in hot water (Naumann); miscible in all proportions with alcohol and ether. From solution in nitric acid of sp. gr. 1·2, or in strong sulphuric acid, it is precipitated by water without alteration; decomposed by heating with sulphuric acid. With zinc, it yields zinc-bromide and butyric acid. Boiled with ammonia, it forms ammonium bromide and amidobutyric acid (Schneider). By supersaturating the acid with soda-ley, evaporating, heating the residue for some time on the water-bath, then supersaturating with sulphuric acid, agitating with ether, and evaporating the latter, a syrupy acid is obtained, which, when saturated with zinc carbonate, yields needles of a salt isomeric or identical with zinc butylactate or oxybutyrate, $(C^4H^7O^3)^2Zn.2H^2O$ (i. 688; iv. 296) (Naumann).

The *metallic bromobutyrates* are mostly soluble in water and in alcohol, and difficult to crystallise. The *lead salt* $(C^4H^6BrO^2)^2Pb$, obtained from the potassium salt by precipitation with neutral lead acetate, is a white pasty precipitate moderately soluble in alcohol. A second lead salt, $(C^4H^6BrO^2)^2Pb.2PbO$, is obtained by evaporating the liquid filtered from the neutral salt, or by precipitating the potassium salt with basic lead acetate. The *silver salt* $C^4H^6BrO^2Ag$ is a white crystalline precipitate, which becomes darker on exposure to light, and is resolved by boiling water into silver bromide and (probably) butylactic acid (Schneider).

Ethyl bromobutyrate, $C^4H^6BrO^2.C^2H^5$, is a colourless, fragrant, heavy, oily liquid of sp. gr. 1·33 at 15°, boiling at about 185°, but with partial decomposition even in a current of carbonic acid gas (Schneider); of sp. gr. 1·345 at 12°, boiling at 175°–178° (Cahours). It is but imperfectly decomposed by boiling with caustic alkalis, but when heated with lead hydrate it yields the lead salt of bromobutyric acid.

Bromisobutyric acid is formed by heating isobutyric acid with bromine to 130°, and forms on cooling a crystalline mass, which may be purified by heating in a stream of carbonic acid gas, pressing, and drying in a vacuum. It melts at 42°, decomposes on distillation, dissolves easily in alcohol and ether, and forms with water a heavy oil, which dissolves when warmed, but separates again on cooling. Heated with caustic baryta it yields barium bromide and the barium salt of iso-oxybutyric acid (perhaps identical with dimethoxalic acid, iv. 274), which when separated from its barium salt by sulphuric acid, is crystallisable, melts at 80°, solidifies at 76°, and sublimes below 100° in long needles (Morkownikoff).

Dibromobutyric acid, $C^4H^6Br^2O^2$, is formed by heating a mixture of 1 mol. (2·5 vol.) butyric acid and 4 at. (3 vol.) bromine (or 1 mol. monobromobutyric acid and

2 at. bromine) to 140°–160° for six or eight hours in strong sealed tubes. After purification it is a light yellow oil having a peculiar aromatic odour, a sp. gr. of 1·97, soluble in 30 pts. water, becoming buttery at −15°, decomposing before it boils (Schneider); boils at 150° under a pressure of 3 mm. of mercury (Friedel a. Machuca). According to Cahours (*Rép. Chim. pure*, iv. 145), dibromobutyric acid obtained as above, crystallises in thin colourless prisms melting at 45°–48°, boils under ordinary pressure at 232°, with partial decomposition, and is converted by treating its alcoholic solution with hydrochloric acid gas, into ethyl dibromobutyrate boiling at 191°–193°. By zinc and dilute sulphuric acid, dibromobutyric acid is converted into butyric acid. Its salts resemble those of monobromobutyric acid. The bromotriconic acid of Cahours, obtained by the action of bromine on potassium citraconate (i. 693), is isomeric, not identical, with dibromobutyric acid (Schneider).

By heating 1 mol. dibromobutyric acid with 4 at. bromine to 150°–180°, there is formed a light brown viscid liquid, which gradually deposits needle-shaped crystals, easily soluble in ether, and probably consisting of tetrabromobutyric acid (Schneider).

Chlorobutyric Acids. *Monochlorobutyric acid*, $C^4H^7ClO^2$, is formed, together with more highly chlorinated products, by passing chlorine into butyric acid containing a little iodine. On distilling the thick liquid thereby produced, till decomposition sets in, a distillate is obtained containing butyric and chlorobutyric acids, and by fractional distillation a portion may be separated which boils at 200°–210°, and on cooling yields monochlorobutyric acid in white prismatic needles. The product is however very small. Chlorobutyric acid dissolves easily in hot water, and crystallises therefrom in slender flexible needles. It melts at 98°–99°, solidifies again at 93°, sublimes at 80° in white iridescent laminæ, and volatilises partially under the air-pump at ordinary temperatures (Morkownikoff, *Zeitschr. f. Chem.* [2] iv. 621).

Dichlorobutyric acid, $C^4H^6Cl^2O^2$, is formed by the action of chlorine on butyric acid in sunshine (i. 694). If the action of the chlorine be assisted by heating the butyric acid, first in the water-bath, afterwards to the boiling point of the acid, a white sublimate is formed in the neck of the retort, consisting of carbon trichloride C^2Cl^6 (Naumann, *Ann. Ch. Pharm.* cxix. 120).

BUTYRIC ALDEHYDE. $C^4H^8O = C\begin{cases}C^3H^7\\ O''\\ H\end{cases}$.—This compound is obtained, together with propionic aldehyde, by heating a mixture of calcium formate and butyrate in equivalent proportions. The product, after treatment with lead oxide and calcium chloride, is resolved by fractional distillation into propionic aldehyde boiling between 54° and 63°, and butyric aldehyde boiling between 73° and 77°, identical therefore with the butyric aldehyde which Guckelberger obtained by oxidation of fibrin, albumin, and casein (i. 689). It has a sp. gr. of 0·8341 at 0°, is less soluble in water than propionic aldehyde, and on exposure to the air is quickly converted into butyric acid. Isobutyl alcohol (from fusel-oil), oxidised with chromic acid, also yields a butyric aldehyde boiling at 70°–78°, together with propionic aldehyde, propionic acid, and butyric acid (Michaelson, *Ann. Ch. Pharm.* cxxxiii. 182). According to Pierre a. Puchot (*Compt. rend.* lxx. 434), butyric aldehyde obtained by oxidation of isobutyl alcohol boils at 74°, and has a sp. gr. of 0·8226 at 0°, 0·7919 at 27·75°, and 0·7638 at 50·4°.

BUTYRYL or **DIBUTYRYL.** $(C^4H^7O)^2 = C^8H^{14}O^2$ (Freund, *Ann. Ch. Pharm.* cxviii. 33).—Produced by the action of sodium-amalgam on butyryl chloride, or of zinc on the same compound mixed with ether. To prepare it, butyryl chloride is gently heated with an amalgam of 1 pt. sodium and 2 pts. mercury, and the viscous mass which separates is freed by distillation from excess of butyryl chloride. On treating the residue with water, an oily layer rises to the surface, consisting of impure butyryl, which may be purified by agitation with solution of potassium carbonate, drying over calcium chloride, and distillation, the portion which goes over between 245° and 260° being collected apart. Butyryl thus obtained is an aromatic oil, slightly soluble or insoluble in water. Heated with potash, it yields potassium butyrate, and an aromatic liquid which passes over on fractional distillation between 175° and 185°, and exhibits the composition of butyrone, $C^7H^{14}O$, but boils at a higher temperature, and does not unite with alkaline bisulphites or with ammonia.

BUTYRYL CHLORIDE or **BUTYRIC CHLORIDE,** C^4H^7OCl, is decomposed at a gentle heat by *sodium-amalgam*, yielding butyryl (or dibutyryl), $C^8H^{14}O^2$; also in ethereal solution by granulated *zinc*, according to the equation:

$$\underset{\text{Butyric chloride.}}{4C^4H^7OCl} + \underset{\text{Ethyl oxide.}}{2(C^2H^5)O} + Zn = ZnCl^2 + \underset{\text{Ethyl chloride.}}{2C^2H^5Cl} + \underset{\text{Ethyl butyrate.}}{2C^4H^7(C^2H^5)O^2} + \underset{\text{Butyryl.}}{C^8H^{14}O^2}$$

(Freund, *Ann. Ch. Pharm.* cxviii. 33.)

With *zinc-ethyl*, it yields ethyl-butyryl or ethyl-propyl ketone (Popoff, *Zeitschr. f. Chem.* [2] iv. 619).

$$2C^3H^7COCl + Zn(C^2H^5)^2 = ZnCl^2 + 2CO\left\{\begin{matrix}C^2H^5\\C^3H^7\end{matrix}\right.$$

Isobutyric chloride, formed, together with isobutyric oxide, by the action of phosphoric oxychloride on sodium isobutyrate, is a colourless liquid, boiling at 92° (butyric chloride boils at 95°), and decomposed by water (Morkownikoff).

BUTYRIC OXIDE or **ANHYDRIDE.** $(C^4H^7O)^2O$. *Preparation* and *properties* (i. 694).—Isobutyric oxide, formed as above mentioned, is a colourless liquid, lighter than water, boiling at 180°–181° (butyric oxide boils at 190°), and converted into isobutyric acid by warming with water (Morkownikoff).

Butyro-hypochlorous Oxide or *Butyrate of Chlorine*, $\left.\begin{matrix}C^4H^7O\\Cl\end{matrix}\right\}O$, isomeric with chlorobutyric acid, is produced by exposing butyric oxide in a well-cooled vessel to the action of gaseous hypochlorous oxide:

$$(C^4H^7O)^2O + Cl^2O = 2(C^4H^7O)ClO.$$

It is a yellowish liquid, which detonates when heated, is slowly decomposed by light, and is analogous in its chemical relations to acetate of chlorine (p. 25) (Schützenberger, *Rép. Chim. pure*, iv. 268). The corresponding *bromine-compound*, $(C^4H^7O)BrO$, a colourless explosive liquid, is produced by the action of bromine on the chlorine-compound (Schützenberger), or on silver-butyrate (Borodine, *Ann. Ch. Pharm.* cxix. 121; *Zeitschr. f. Chem.* [2] v. 342).

Tributyro-hypoiodous Oxide or *Iodine Tributyrate*, $\left.\begin{matrix}(C^4H^7O)^3\\I^{'''}\end{matrix}\right\}O^3$, is formed by mixing iodine chloride with an equivalent proportion of sodium, potassium, or zinc butyrate, or by gradually adding iodine to butyro-hypochlorous oxide, or better by passing hypochlorous oxide into butyric oxide mixed with iodine till the latter disappears. The resulting flocculent precipitate dissolved in acetic oxide at 60°, crystallises therefrom in slender white needles. It is not altered by light, but when heated is quickly decomposed into iodine, carbon dioxide, and propyl butyrate (Schützenberger).

BUXINE. See BEBIRINE (p. 255).

C

CADMIUM. On the extraction of cadmium from zinc-blende at Engis in Belgium, see Städeler (*J. pr. Chem.* xci. 359; *Jahresb.* 1864, 759).

The solution of cadmium in acids is greatly facilitated by addition of a small quantity of platinic chloride. The combination of cadmium with bromine and iodine is likewise facilitated by the presence of platinum (Alberts, *Jahresb.* 1865, p. 242).

The following table exhibits the solubility of cadmium chloride and iodide at different temperatures, as determined by Kremers (*Pogg.* ciii. 57; *Jahresb.* 1858, p. 40):

	At 20°	40°	60°	80°	100°	
1 pt. $CdCl^2$ dissolves in	0·71	0·72	0·72	0·70	0·67	pt. water
„ CdI^2 „	1·08	1·00	0·93	0·86	0·75	„

Respecting the specific gravities of solutions of cadmium chloride, bromide, and iodide of various strengths and at different temperatures, see Kremers (*Jahresb.* 1858, p. 41; 1859, p. 49; 1860, p. 46).

Cadmium oxide may be obtained in red crystals, apparently cubic, by heating the amorphous oxide to whiteness for two or three hours in a porcelain tube through which a stream of oxygen is passed. The oxide melts, volatilises, and condenses at the cold end of the tube; the best crystals are obtained by placing a plug of asbestos at that end (Sidot, *Zeitschr. f. Chem.* [2] v. 606).

A compound of cadmium oxide with *potassium oxide* is obtained by saturating fused potassium hydrate with cadmium oxide, and adding cold potash-ley to the fused mass till the resulting precipitate becomes permanent. The solution on cooling yields crystals of potassium hydrate enclosing the potassio-cadmic oxide, and on dissolving them in water, the latter compound remains in hydrated crystalline scales having a pearly lustre and the colour of lead iodide. It is insoluble in water, but is decomposed by prolonged contact with water, with separation of cadmium hydrate (St. Meunier, *Compt. rend.* lxiii. 330).

CÆSIUM. Occurrence, and separation from rubidium (i. 1113; iv. 126).

Stannic chloride added to a solution of the chlorides of sodium, potassium, lithium, rubidium, and cæsium containing free hydrochloric acid, forms a heavy white precipitate consisting of nearly pure *cæsio-stannic chloride*, $Sn^{iv}Cs^2Cl^6$; and by dissolving this precipitate in hot water acidulated with hydrochloric acid, evaporating till crystals form on the surface, and leaving the solution to cool, the salt is obtained perfectly pure. This reaction affords an easy method of detecting cæsium in a mixture of alkaline chlorides, and of preparing pure cæsium-compounds; but it is not adapted for quantitative analysis, as the precipitate is not formed in a neutral solution, and is soluble to a slight extent in concentrated hydrochloric acid (J. P. Sharples, *Sill. Am. J.* [2] xlvii. 178).

According to Debray (*Bull. Soc. Chim.* [2] v. 404), cæsium—as well as potassium, rubidium, and thallium—is precipitated by phosphomolybdic acid.

CAFFEIDINE. See the next article.

CAFFEINE or **THEINE.** $C^8H^{10}N^4O^2$.—This base has the composition of methyl-theobromine, $C^7H^7(CH^3)N^4O^2$, and may be formed synthetically by treating the silver-compound of theobromine (v. 761) with methyl-iodide:

$$C^7H^7AgN^4O^2 + CH^3I = AgI + C^7H^7(CH^3)N^4O^2$$

(Strecker, *Ann. Ch. Pharm.* cxviii. 151). For the relations between xanthine, theobromine, and caffeine, see XANTHINE (v. 1051).

Caffeine has been found in the seeds of the Kola-tree of West Central Africa (*Cola acuminata*) to the amount of 2·13 p. c. of the dried seed (Attfield, *Pharm. J. Trans.* [2] vi. 257).

C. Grosschoff (*Jahresb.* 1866, 471) describes a method of preparing caffeine on the large scale from tea, by heating the concentrated aqueous decoction with litharge, evaporating the decanted liquid to a syrup, and treating it with pearlash and alcohol.

To estimate the amount of caffeine in tea-leaves, Claus (*Jahresb.* 1863, p. 708) exhausts them with ether; distils off two-thirds of the ether; agitates the residue repeatedly with dilute sulphuric acid; supersaturates the colourless caffeine-solution with magnesia; evaporates to dryness; and extracts the caffeine from the residue by ether, which on evaporation leaves it in white crystals. Tea-leaves, after exhaustion with ether, still yield a small quantity of caffeine to alcohol. Claus finds that the inferior commercial sorts of tea are richer in caffeine than the finer and more fragrant sorts.

Caffeine evaporated to dryness with a little *chlorine-water* yields a purple-red residue which becomes golden-yellow when more strongly heated, but red again on addition of ammonia. By this reaction, caffeine may be detected even in a single coffee-bean (Schwarzenbach, *Jahresb.* 1861, p. 871; 1865, p. 730). Caffeine forms with *phosphomolybdic* acid a yellow precipitate which dissolves without colour in ammonia (J. Trapp, *ibid.* 1863, p. 702).

Iodine-compounds of Caffeine (Tilden, *Chem. Soc. J.* [2] iii. 99; iv. 145).—A solution of caffeine in dilute alcohol strongly acidulated with *hydriodic acid* deposits after a few days, especially in sunshine, long prisms of caffeine hydrotri-iodide, $2(C^8H^{10}N^4O^2.HI^3).3H^2O$, having a green metallic lustre and exhibiting the same polarising properties as Herapath's sulphate of iodoquinine. Caffeine ethyl tri-iodide, $C^8H^{10}N^4O^2.C^2H^5I^3$, is formed on heating caffeine with *ethyl iodide* to 130° for about four hours, evaporating at a gentle heat, mixing the residue with a solution of iodine in hydriodic acid, and recrystallising the resulting precipitate from alcohol. It forms brown shining scales permanent at 100°. When caffeine is heated for a shorter time with ethyl iodide, part of it remains unaltered, and after the ethyl-caffeine has been precipitated with iodine, the solution deposits monohydrated caffeine hydrotri-iodide, $C^8H^{10}N^4O^2.HI^3 + H^2O$, in shining crystals. *Methyl-iodide* forms with caffeine the compound $C^8H^{10}N^4O^2.CH^3I$, which dissolves easily in water, and when mixed in aqueous solution with tincture of iodine, is converted into the tri-iodated compound

The rate of expansion by heat of solutions of calcium chloride of various strengths has been determined by Gerlach (*Jahresb.* 1859, p. 47). The following table shows the volumes at different temperatures of solutions of this salt containing in 100 pts. the quantities of salt standing at the heads of the several columns, the volume of each solution at 0° being taken as unity. The last number (bracketed) in each column denotes the boiling point of the solution:

CALCIUM CHLORIDE.

	10	20	30	40
0°	1·0000	1·0000	1·0000	1·0000
10	1·0017	1·0027	1·0033	1·0043
20	1·0043	1·0060	1·0072	1·0089
30	1·0075	1·0096	1·0114	1·0136
40	1·0112	1·0139	1·0159	1·0183
50	1·0155	1·0183	1·0205	1·0231
60	1·0205	1·0231	1·0252	1·0280
70	1·0259	1·0280	1·0300	1·0329
80	1·0314	1·0330	1·0348	1·0377
90	1·0373	1·0382	1·0397	1·0424
100	1·0429	1·0432	1·0447	1·0472
	1·0442	1·0456	1·0496	1·0557
	(101·4°)	(104·2°)	(109·7°)	(118°)

On the rate of expansion of solutions of calcium chloride, bromide, and iodide, see also Kremers (*Jahresb.* 1858, p. 40; 1859, p. 49).

The following methods of preparing calcium iodide are recommended by R. Wagner (*Chem. Centr.* 1863, p. 143; *Jahresb.* 1862, p. 132): 1. Addition of iodine to an aqueous pulp of calcium sulphite and hydrate.—2. Addition of iodine, to saturation, to calcium hyposulphite stirred up with water, whereby a mixture of calcium iodide and tetrathionate is formed, which may be used for technical purposes (chlorimetry for example) instead of potassium iodide.—3. Mixing of iodine, finely divided or dissolved in hydriodic acid or potassium iodide, with calcium nitrite and hydrate, whereby calcium iodide and nitrate are produced:

$$(NO^2)^2Ca + 2CaH^2O^2 + 2I^2 = (NO^3)^2Ca + 2CaI^2 + 2H^2O.$$

The last portions of nitrite are not however converted into nitrate.—4. Addition of finely divided iodine to a concentrated mixture of arsenious oxide and milk of lime. The iodine then dissolves, with formation of insoluble arsenate, and soluble iodide of calcium. When the reaction is complete, the filtered solution of calcium iodide is quite free from arsenic. The arsenious oxide may be replaced by antimonious oxide (precipitated from the chloride by sodium carbonate).

For Liebig's method of preparing calcium iodide, and applying it to the preparation of potassium iodide, see POTASSIUM IODIDE (iv. 704).

Calcium Oxysulphide.—According to P. W. Hoffmann (*Compt. rend.* lxii. 291), a non-ignited mixture of 2 mol. calcium sulphide and 1 mol. lime does not form oxysulphide when boiled with water; but at a red heat the same mixture is converted into an oxysulphide having the composition $2CaS.CaO$, any larger addition of lime remaining uncombined. This oxysulphide is contained in recently lixiviated soda residues.

Alloy of Calcium and Zinc.—Calcium fused with a large excess of zinc forms an alloy, $CaZn^{12}$, which crystallises in quadratic octohedrons of sp. gr. 6·37. It is decomposed by water (G. vom Rath, *Zeitschr. f. Chem.* [2] v. 665).

CALCULUS OF CHEMICAL OPERATIONS. See List of Memoirs at the end of the article CHEMICAL ACTION.

CAMPHOCARBONIC ACID. $C^{11}H^{16}O^3 = C^{10}H^{16}O.CO^2$.—When a solution of camphor in a hydrocarbon (toluene or benzene) is treated with sodium, the metal dissolves without evolution of hydrogen, and a solution is formed containing sodium camphor and sodium borneol:

$$\underset{\text{Camphor.}}{2C^{10}H^{16}O} + Na^2 = \underset{\text{Sodium camphor.}}{C^{10}H^{15}NaO} + \underset{\text{Sodium borneol.}}{C^{10}H^{17}NaO}$$

On passing a stream of carbon dioxide into this solution, both of these compounds take up CO^2, forming sodium camphocarbonate, $C^{11}H^{15}NaO^3$, and sodium borneolcarbonate, $C^{11}H^{17}NaO^3$; and if the resulting magma be treated with water, both salts dissolve, but the latter immediately begins to decompose, with separation of borneol; so that the aqueous solution decanted from the hydrocarbon becomes turbid and gradually deposits borneol. The camphocarbonate, on the other hand, remains undecomposed, and its clear aqueous solution separated from the borneol yields with hydrochloric or sulphuric acid a white precipitate of camphocarbonic acid.

This acid is sparingly soluble in water, easily in alcohol and ether, permanent at ordinary temperatures, melts at 118°–119°, but begins to decompose even at this temperature; but on attempting to distil it at a stronger heat, it is completely resolved into camphor and carbon dioxide. After being once fused, it melts at a much lower temperature; in fact a mixture of the pure acid with camphor melts below 100°. Camphocarbonic acid is monobasic; its lead salt is insoluble in water and in acetic acid (Baubigny, *Zeitschr. f. Chem.* [2] iv. 481, 647).

CAMPHOLIC ACID. $C^{10}H^{18}O^2$.—According to Malin (*Ann. Ch. Pharm.* cxlv. 200), the potassium salt of this acid is produced by adding potassium in small pieces to a boiling solution of camphor in 3 pts. of petroleum. This salt crystallises by evaporation in a vacuum in laminar crystals containing $C^{10}H^{17}KO^2.2H^2O$. The acid separated from it by hydrochloric acid forms white lumpy flocks, which may be purified by recrystallisation from alcohol or by distillation.

CAMPHOR. $C^{10}H^{16}O$.—Ordinary camphor—the camphor of the Lauraceæ—might be regarded, so far as its composition is concerned, as the aldehyde of borneol, $C^{10}H^{18}O$, and it is produced by oxidising borneol with nitric acid. Nevertheless, it does not exhibit the characters of an aldehyde; for, as shown by Fittig a. Tollens (*Ann. Ch. Pharm.* cxxix. 371), it does not unite with alkaline bisulphites; it is not converted into borneol by nascent hydrogen, nor into camphic acid, $C^{10}H^{16}O^2$, by direct oxidation with nitric acid (the products of that reaction being camphoric acid, $C^{10}H^{16}O^4$, and camphretic acid, $C^8H^8O^4$); and it is not oxidised by a mixture of potassium dichromate and sulphuric acid, even when heated therewith for a long time in sealed tubes.

Camphor, or a substance isomeric with it, is formed, together with other products, by oxidising rectified turpentine-oil with aqueous potassium permanganate, or by atmospheric oxidation of camphene, $C^{10}H^{16}$ (prepared from the monohydrochloride, $C^{10}H^{16}.HCl$), in contact with platinum-black, also by chromic acid (Berthelot, *Compt. rend.* xlvii. 266; lxiv. 35; *Jahresb.* 1858, p. 441; 1867, p. 337; *Ann. Ch. Pharm.* cl. 374).

The crystals of camphor belong to the hexagonal system. Well-defined crystals obtained by very slow sublimation at ordinary temperatures exhibited the combination oP . ∞P . P; angle oP : P = 118·9° (Descloizeaux, *Ann. Ch. Phys.* [3] lvi. 219).

Reactions.—1. The oil obtained by the dry distillation of camphor in contact with clay (i. 728) is a mixture of cymene with unaltered camphor (Kraut, *J. Pharm.* [3] xlv. 105).—2. Camphor distilled with *zinc chloride* yields, not merely cymene, as supposed by Gerhardt, but a mixture of several hydrocarbons of the aromatic series. The distillate, freed as completely as possible from undecomposed camphor by repeated distillation with zinc chloride, is resolved by fractional distillation (the portions boiling above 150° being distilled over sodium) into the following products: α. Below 100° a small quantity of liquid containing oxygenated products (apparently including acetone), and perhaps a little benzene.—β. From 108° to 112°, chiefly toluene.—γ. From 138° to 143°, xylene.—δ. From 164° to 167°, pseudocumene or trimethylbenzene (p. 296).—ε. From 173° to 176°, cymene with a small quantity of pseudocumene.—ζ. From 185° to 188°, laurene, $C^{11}H^{16}$ (Fittig, Köbrich, a. Jilke, *Ann. Ch. Pharm.* cxlv. 129). According to Lippman a. Louguinine (*Zeitschr. f. Chem.* [2] v. 413), the portion of the distillate boiling between 140° and 240° contains also cresol, C^7H^8O, which may be dissolved out from it by potash; also phenol (Rommier, *Compt. rend.* lxviii. 930).—3. Camphor heated with *phosphorus pentasulphide* is almost wholly resolved into water and cymene (R. Pott, p. 302):

$$5C^{10}H^{16}O + P^2S^5 = 5C^{10}H^{14} + P^2O^5 + 5H^2S.$$

4. Camphor triturated with an equivalent quantity of *phosphorus pentachloride* is converted into a semifluid mass, which is resolved by very slow distillation into hydrochloric acid and cymene:

$$C^{10}H^{16}O + PCl^5 = C^{10}H^{15}Cl + HCl + POCl^3$$

and

$$C^{10}H^{15}Cl = HCl + C^{10}H^{14}$$

(Louguinine a. Lippmann, *Bull. Soc. Chim.* [2] vii. 374).

5. For the reaction of camphor with *nitric acid* and with *chromic acid*, see the commencement of this article.

6. Camphor heated to 200° with concentrated *hydriodic acid* gives off a mixture of three hydrocarbons, viz. C^8H^{16}, boiling at 135°–140°; $C^{10}H^{18}$, boiling at 163°; and $C^{10}H^{20}$, at 170°–175°. The two former take up bromine without giving off hydrobromic acid, and are easily oxidised, $C^{10}H^{18}$ yielding thereby acetic acid, together with three other acids (Weyl, *Zeitschr. f. Chem.* [2] iv. 496).

Brominated Derivatives of Camphor.—Camphor unites directly with bromine, forming a compound $C^{10}H^{16}O.Br^2$, easily decomposed by heat, by ammonia, and even by contact with the air (Laurent). Th. Swarts (*Instit.* 1862, p. 63) prepares this compound by mixing a saturated solution of camphor in chloroform with an equivalent quantity of bromine; the compound then partly separates after a few hours as a red powder, and the remainder is deposited from the mother-liquor in beautiful orange-coloured prisms.

The bromide $C^{10}H^{16}OBr^2$ is resolved by heating to 100° in sealed tubes (Swarts), or by distillation (Perkin, *Chem. Soc. J.* [2] iii. 22), into hydrobromic acid and monobromocamphor, $C^{10}H^{15}BrO$. This compound may also be produced directly by heating bromine and camphor in sealed tubes for three hours in the water-bath (Swarts). It crystallises in transparent prisms very much like those of ordinary sodium sulphate, having a faint odour of camphor, and a turpentine-like taste; dissolves easily in alcohol and ether; melts at about 76° and solidifies at 74°, or when left at rest, sometimes not till cooled to 54° (Perkin), to 36° (Swarts); boils at 274° (Perkin; Swarts). It is not decomposed by alcoholic potash (Swarts). Heated with alcoholic ammonia to 180°, it decomposes to a slight extent, with formation of ammonium bromide and a peculiar base (Perkin). It unites with hydrobromic acid, forming an oily compound, $6C^{10}H^{15}BrO.HBr$. Heated with bromine to 120° in a sealed tube, it forms, together with hydrobromic acid, an oil the alcoholic solution of which, when decolorised by animal charcoal, deposits shining prisms of dibromocamphor, $C^{10}H^{14}Br^2O$. This latter compound smells like turpentine, has a bitter taste, is insoluble in water, and less soluble in alcohol than camphor or the monobrominated compound. It melts at 114·5°, becomes liquid even under boiling water, and distils with partial decomposition at 285° (Swarts, *Zeitschr. f. Chem.* [2] ii. 628).

Chlorocamphor, $C^{10}H^{15}ClO$, is produced by gradually adding camphor to a moderately concentrated solution of hypochlorous acid, and falls to the bottom as a liquid which ultimately solidifies:

$$C^{10}H^{16}O + HClO = H^2O + C^{10}H^{15}ClO.$$

After several recrystallisations from dilute alcohol, it forms white indistinct crystals having the smell and taste of camphor, and nearly insoluble in water. It melts at 95°, decomposes at about 200°, with evolution of hydrochloric acid; is but slowly attacked by nitric acid, even at the boiling heat; and dissolves without alteration in strong sulphuric acid at ordinary temperatures. Its alcoholic solution mixed at the boiling heat with silver nitrate yields a precipitate of silver chloride (Wheeler, *Sill. Am. J.* [2] xlv. 48).

Oxycamphor, $C^{10}H^{16}O^2$, isomeric or perhaps identical with camphic acid, is produced (together with two other non-chlorinated compounds not yet isolated) by heating chlorocamphor for several hours with alcoholic potash. It crystallises from alcohol in white needles melting at 137°, distils with vapour of water, may be sublimed without decomposition, and has the smell and taste of camphor (Wheeler).

Sodium-camphor. $C^{10}H^{15}NaO$.—When a solution of camphor in an inert hydrocarbon (toluene, for example) is carefully heated with sodium to 90°, the sodium dissolves, forming a mixture of sodium-camphor and sodium-borneol:

$$2C^{10}H^{16}O + Na^2 = C^{10}H^{15}NaO + C^{10}H^{17}NaO.$$

The solution on cooling deposits very unstable crystals of sodium-camphor (Baubigny, *Zeitschr. f. Chem.* [2] ii. 408; iv. 298). According to Malin (*Jahresb.* 1867, p. 724), a boiling solution of camphor in petroleum treated with potassium yields, on evaporation in a vacuum, crystals of potassium campholate, $C^{10}H^{17}KO^2$. If this statement be correct, cymene should also be formed, according to the equation $2C^{10}H^{16}O = C^{10}H^{18}O^2 + C^{10}H^{14}$; but the formation of this hydrocarbon was not actually observed; on the other hand, borneol was found to be produced.

The mixture of sodium-camphor and sodium-borneol obtained as above yields, when treated with alcoholic iodides, the corresponding alcoholic derivatives of camphor and borneol. *Ethyl-camphor*, $C^{10}H^{15}(C^2H^5)O$, is obtained by treating this mixture, or the crystals of sodium-camphor dissolved in a hydrocarbon, with ethyl iodide, washing the product with water, distilling off the hydrocarbon, cooling the residue to −20° to separate the greater part of the unaltered camphor, and subjecting the remaining liquid to fractional distillation. It is a colourless liquid insoluble in water, soluble in alcohol and ether, boiling between 226° and 229°, having a sp. gr. of 0·946 at 22°, and a dextrogyrate power of about 161·4° for the transition tint (Baubigny).

The portion of the crude liquid obtained in the preparation of ethyl-camphor which distils between 195° and 210°, yields by repeated treatment with sodium, followed each time by distillation, the ethyl-derivative of borneol, $C^{10}H^{17}(C^2H^5)O$. These ethylated derivatives of camphor and borneol are not attacked by phosphorus pentachloride at ordinary temperatures; ethyl-camphor is slowly acted upon at 100°, yielding a small quantity of ethyl chloride. Ethyl-camphor is insoluble in cold nitric acid, but dissolves at 100°, and separates out unaltered on cooling. Ethyl-borneol, on the other hand, is decomposed by nitric acid at ordinary temperatures with evolution of nitrous acid vapours, the acid solution depositing camphor when mixed with water (Baubigny, *Zeitschr.* [2] iv. 481).

Amyl-camphor, $C^{10}H^{15}(C^5H^{11})O$, obtained by treating the mixture of sodium-camphor and sodium-borneol with amyl iodide, boils at 277·5° (corr.) and has a dextro-rotatory power of 59·4°. Amyl-borneol could not be isolated from the product of the reaction.

The same mixture of sodium-compounds treated with methyl-iodide yields, on the other hand, methyl-borneol, $C^{10}H^{17}(CH^3)O$, but no methyl-camphor.

The same mixture treated with acetic anhydride, glacial acetic acid, or acetic chloride, yields acetyl-borneol, $C^{10}H^{17}(C^2H^3O)O$, which is optically inactive, and is resolved by potash-ley into borneol and acetic acid. No acetyl-camphor appears to be formed in either case (Baubigny, *Zeitschr.* [2] iv. 299, 481).

When the product of the action of sodium on camphor is treated with *ethylene bromide*, no ethylene derivatives are formed, but the ethylene bromide is decomposed in the same manner as when it is treated with alcoholic potash, yielding bromethylene, which by further reaction on the sodium-compounds is converted into acetylene, while camphor and borneol are set free:

$$C^{10}H^{15}NaO + C^{10}H^{17}NaO + 2C^2H^4Br^2 = 2NaBr + 2C^2H^3Br + C^{10}H^{16}O + C^{10}H^{18}O$$

and

$$C^{10}H^{15}NaO + C^{10}H^{17}NaO + 2C^2H^3Br = 2C^2H^2 + C^{10}H^{16}O + C^{10}H^{18}O + Br^2.$$

When a stream of carbonic acid gas is passed to saturation into the mixture of sodium-compounds obtained as above, the sodium salts of camphocarbonic acid, $C^{11}H^{16}O^3$, and borneol-carbonic acid, $C^{11}H^{18}O^3$, are produced by direct addition of CO^2. On adding water to the product, the sodium salts dissolve, and the aqueous solution, if immediately separated by decantation from the hydrocarbon, soon becomes turbid, and gradually yields an abundant precipitate of borneol, resulting from the decomposition of the very unstable borneol-carbonic acid; this reaction affords indeed an easy way of preparing borneol. The aqueous solution separated from the borneol contains the sodium camphocarbonate, and when mixed with sulphuric or hydrochloric acid, yields a precipitate of camphocarbonic acid (Baubigny, *Zeitschr.* [2] iv. 482, 647).

CAMPHOR RESIN. Camphor heated for three or four hours with alcoholic potash is partly converted into a soft tough golden-yellow resin, $C^{20}H^{30}O^2$, which becomes perfectly inodorous after prolonged heating to 100° (L. Barth, *Zeitschr. f. Chem.* [2] iii. 508).

CAMPHORIC ACID. $C^{10}H^{16}O^4$.—Blumenau (*Ann. Ch. Pharm.* lxvii. 119) observed that when the crude acid produced by oxidising camphor with nitric acid was heated very strongly to expel the latter, a viscous mass was produced, which he regarded as an isomeric modification of camphoric acid. Monoyer has, however, shown (*J. Pharm.* [3] xlv. 177) that this substance consists of camphoric oxide or anhydride, $C^{10}H^{14}O^3$. To prepare camphoric acid, Monoyer boils camphor with 10 pts. of strong nitric acid and a few platinum-cuttings, renewing the acid from time to time till the supernatant oily layer disappears; then distils off the excess of nitric acid; and heats the camphoric acid, which crystallises out in cooling, till white fumes begin to appear. The residual mixture of camphoric acid with a small quantity of the oxide may be wholly converted, either into the acid by boiling with water, or into the anhydride by distillation. If the same mixture be dissolved in hot alcohol, the solution yields on cooling, especially if a little water be added, nothing but camphoric oxide.

Camphoric oxide treated with barium dioxide and water, is converted into the barium-compound of camphoric peroxide, $C^{10}H^{14}BaO^6$ (Brodie; see iv. 311).

Camphoric acid heated to 200° with concentrated hydriodic acid, yields, together with carbon dioxide and free iodine, a hydrocarbon, C^9H^{18}, which does not unite with bromine, and is oxidised by prolonged heating with chromic acid mixture, to an insoluble acid which crystallises in colourless needles (Weyl, *Zeitschr. f. Chem.* [2] iv. 496).

The camphorates of the alkali-metals yield by dry distillation, phorone or camphorone, $C^9H^{14}O$ (i. 733); but when fused with excess of caustic alkali, they yield chiefly three products, all of which are acids, one volatile consisting of butyric acid (perhaps mixed with valeric), and two fixed—viz. a crystalline acid melting at 114°, and exhibiting the composition of pimelic acid, $C^7H^{12}O^4$, and a liquid acid resembling Schwanert's camphretic acid (Hlasiwetz a. Grabowski, *Zeitschr. f. Chem.* [2] iv. 508).

Potassium camphorate, $C^{10}H^{14}O^4K^2$, obtained by saturating a boiling solution of potassium carbonate with camphoric acid, crystallises with difficulty in tufts of deliquescent crystals soluble in alcohol. The *sodium salt* $C^{10}H^{14}O^4Na^2$ prepared in like manner forms indistinct crystals which deliquesce in moist air. The *lithium salt* $C^{10}H^{14}O^4Li^2$ is a white powder soluble in an equal weight of water, soluble also in alcohol. Acid camphorates of the alkali-metals have not been obtained.

Barium salts.—By boiling camphoric acid with excess of barium carbonate, an acid and a neutral salt are formed together, the acid salt crystallising out first. The *neutral salt* $2C^{10}H^{14}O^4Ba.9H^2O$ crystallises in wavellitic needles, soluble in an equal weight of water, sparingly soluble in alcohol, becoming anhydrous at 120°. The *acid salt* $(C^{10}H^{15}O^4)^2Ba.2H^2O$, or $C^{10}H^{14}O^4Ba.C^{10}H^{16}O^4.2H^2O$, obtained as above, or by dissolving camphoric acid in an equivalent quantity of the neutral salt, crystallises in tufts of prisms soluble in 50 pts. of boiling and 120 pts. of cold water. When heated it gives off part of the camphoric acid, which sublimes. *Calcium salts.*—The *neutral salt* $2C^{10}H^{14}O^4Ca.9H^2O$ is obtained by treating camphoric acid with milk of lime, in crystalline crusts soluble in 12 to 15 pts. water. The *acid salt* $(C^{10}H^{15}O^4)^2Ca$ is obtained in large anhydrous prismatic crystals by boiling the neutral salt with camphoric acid, evaporating to dryness, and crystallising the residue from aqueous solution. A *hydrated acid salt*, $(C^{10}H^{15}O^4)^2Ca.7H^2O$, was once obtained in crystalline crusts by boiling calcium carbonate with aqueous camphoric acid, evaporating to dryness, and crystallising the redissolved residue. By again boiling this last salt with calcium carbonate, crystalline crusts or prismatic crystals were formed, soluble in 15 pts. water, and agreeing approximately with the formula $2C^{10}H^{14}O^4Ca.(C^{10}H^{15}O^4)^2Ca.8aq$. The *magnesium salt* $C^{10}H^{14}O^4Mg$, produced by heating aqueous camphoric acid with magnesia alba, crystallises, apparently under similar circumstances, with 7½, 12, and 13½ mol. water. The 7½-hydrate forms thin efflorescent tables soluble in 2·5 pts. water at 20°, and becoming anhydrous at 120°. A dilute solution of the neutral salt mixed with camphoric acid deposits the latter without forming an acid magnesium salt. The *zinc salt* $C^{10}H^{14}O^4Zn$, obtained by precipitation, is a white sparingly soluble powder (R. Kemper, *Arch. Pharm.* [2] cx. 106; cxvii. 23; *Jahresb.* 1862, p. 270; 1864, p. 403). *Cupric camphorate* heated to 200° gives off, together with camphoric anhydride and water, a hydrocarbon which, after rectification over sodium, has the composition C^8H^{14}, boils at 105°, has a density of 0·793, vapour-density 3·984; smells like camphor and turpentine-oil; is converted by hydrochloric acid gas into a green oil of small volatility; and is resinised by nitric acid (Moitessier, *Jahresb.* 1866, p. 410).

Inactive Camphoric Acid—Paracamphoric Acid—is produced by oxidation of optically inactive camphor (i. 729), or by mixing equal weights of dextro-camphoric and lævo-camphoric acids in concentrated alcoholic solution; in the latter case a rise of temperature takes place, amounting sometimes to 30°, and the inactive acid separates as a white precipitate.

Paracamphoric acid crystallises with difficulty in forms belonging to the monoclinic system, but not exhibiting hemihedral faces. It is less soluble than either of the optically active camphoric acids; 100 pts. alcohol dissolve 33 pts. of it; 100 pts. ether 28 pts.; 100 pts. water only 1 pt.; and in chloroform it is still less soluble. The paracamphorates of the alkali-metals are easily soluble and uncrystallisable. The barium salt forms needle-shaped crystals, soluble in about 10 pts. of water.

When 10 pts. of paracamphoric acid are boiled with 20 pts. absolute alcohol and 5 pts. sulphuric acid, and the liquid then mixed with water, a viscid oil separates, which is resolved by heat into ethyl paracamphorate and paracamphoric anhydride. On dissolving the mixture in boiling alcohol, the anhydride crystallises out, while the ether remains in solution, and may be precipitated by water. *Paracamphoric anhydride* crystallises from chloroform in small needles; 100 pts. chloroform dissolve 25 pts. of it; 100 pts. ether, 4 pts.; 100 pts. alcohol, only 1½ pt. *Ethyl paracamphorate* is a colourless strong-smelling oil, having a sp. gr. of 1·03 at 15°, and boiling at 270°–275°. Boiling potash-ley decomposes it, with formation of an inactive camphoric acid, different from that which was employed in its preparation, being pulverulent, uncrystallisable, nearly insoluble, fusible, and subliming partially with loss of water (Chautard, *Compt. rend.* lvi. 698; *Jahresb.* 1863, p. 394).

CAMPHRENE. $C^9H^{14}O$.—A product isomeric with phorone, formed by the action of sulphuric acid upon camphor. It was first obtained by Chautard (who assigned to it the formula $C^9H^{12}O$, i. 727), and has been further examined by Schwanert (*Ann. Ch. Pharm.* cxxiii. 298). To prepare it, 1 pt. of camphor is heated to 100° for five or six hours with 4 pts. sulphuric acid; the resulting solution is mixed with water; the oil which rises to the surface is distilled: and the portion which goes over between 220° and 240° (the distillate of lower boiling point containing a larger proportion of unaltered camphor) is heated nearly to its boiling point in a stream of hydrogen for four or five days, or till no more camphor is deposited on the neck of the retort, then rectified, the portion boiling between 230° and 235° being collected apart.

Camphrene is a nearly colourless liquid having a pleasant aromatic odour and a sharp taste, a sp. gr. of 0·9614 at 20°; optically inactive; insoluble in water, easily soluble in alcohol and ether. From phorone, which resembles it in its chemical reactions, it is distinguished chiefly by its boiling point, which is from 27° to 30° higher than that of phorone (208°); a similar difference of boiling point is exhibited also by the corresponding derivatives of the two. Both phorone and camphrene are converted by phosphoric anhydride into hydrocarbons having the composition of cumene, C^9H^{12}, that from phorone boiling at 150°–160°, that from camphrene at 170°–175°. Both camphrene and phorone are oxidised by nitric acid to camphrenic acid.

Methyl-camphrene, $C^9H^{13}(CH^3)O$, is formed by adding sodium to a mixture of equal parts of camphrene and benzene in an atmosphere of hydrogen, till the sodium remains unaltered even when heated, and cohobating the solution with excess of methyl iodide. Water added to the resulting liquid separates a brown oil, from which, by repeated rectification, methyl-camphrene is obtained as a colourless aromatic liquid boiling at 225°–230°.

Acetyl-camphrene is obtained in like manner, using acetyl chloride instead of methyl iodide. It is a yellowish viscid liquid, having an unpleasant odour, a sp. gr. of 0·954 at 18°, and boiling at 230°–240°. Its analysis leads to the formula $C^{18}H^{27}(C^2H^3O)O^2$, from which it may be inferred that the true formula of camphrene is $C^{18}H^{28}O^2$, and that of methyl-camphrene $C^{18}H^{26}(CH^3)^2O^2$. This double formula of camphrene is quite consistent with the difference of boiling point between camphrene and phorone, which seems to indicate that these compounds are polymeric with one another, rather than merely isomeric.

CAMPHRENIC ACID. $C^9H^8O^4$? (Schwanert, *loc. cit.*).—Produced, by treating camphrene or phorone for a considerable time with 3 or 4 pts. of strong nitric acid, as a resinous mass which may be purified by solution in sodium carbonate, precipitation with an acid, and evaporation of the alcoholic solution, after decolorisation with animal charcoal. It is white or pale yellow, tasteless and inodorous, nearly insoluble in water, easily soluble in alcohol and ether, and crystallises in microscopic nodules. Heated to 250° it suffers partial carbonisation, and gives off the anhydride $C^9H^6O^3$, in white feathery crystalline groups. The *barium salt* $C^9H^6O^4Ba$ is a brownish-yellow amorphous mass easily soluble in water. The *lead salt* $C^9H^6O^4Pb$, and the *silver salt* $C^9H^6O^4Ag^2$, are white precipitates.

CAMPHRETIC ACID. $C^{10}H^{14}O^7$?—An acid occurring, according to Schwanert (*Ann. Ch. Pharm.* cxxviii. 77), amongst the products obtained by heating camphor with dilute nitric acid, and yielding by dry distillation pyrocamphretic acid, $C^{10}H^{14}O^4$, in the form of an oil; metacamphretic acid, $C^{10}H^{10}O^5$, in tabular crystals; and a sublimate of camphoric anhydride (iv. 756). The existence of this acid is, however, by no means well established. The acid itself and all its salts and ethers are uncrystallisable, and therefore their analyses are not much to be depended upon.

CAMPHRYL CHLORIDE, $C^9H^{13}Cl$, is produced by the action of phosphorus pentachloride on camphrene. The distillate, washed with water and sodium carbonate and repeatedly rectified, yields camphryl chloride as a colourless neutral liquid of sp. gr. 1·038 at 14° and boiling at 205°. The isomeric compound, phoryl or camphoryl chloride, boils at 175°. Camphryl chloride is not decomposed by sodium ethylate (Schwanert, *Ann. Ch. Pharm.* cxxiii. 298).

CANADOL. A term applied by H. Vohl to that portion of the volatile hydrocarbons of Canadian and Pennsylvanian petroleum which boils at 60° and has a sp. gr. of 0·650 to 0·700. This liquid is recommended by Vohl, instead of carbon bisulphide, for extracting the fixed oils of seeds (*Dingl. pol. J.* clxxii. 319; *Jahresb.* 1866, p. 893).

CANARIUM. The fixed oil of the East Indian plant, *Canarium commune*, contains about 51 p. c. oleïn and 49 p. c. stearin and myristin. The oleic acid obtained from it by saponification is identical with that from olive oil (Oudemans, *J. pr. Chem.* xcix. 407).

CANAŪBA WAX. This wax, which forms a coating on the leaves of the Canaüba tree of Brazil (*Copernicia cerifera*), has been investigated by Maskelyne (*Chem. Soc. J.* [2] vii. 87). It is light yellow with a tinge of green; considerably harder than beeswax at ordinary temperatures; melts at about 84°; has a sp. gr. of 0·99907; and leaves about 0·14 p. c. ash when burnt. By saponification with alcoholic potash it yields a considerable quantity of myricyl alcohol, ($C^{30}H^{62}O$ or $C^{31}H^{64}O$), melting at about 88°, which exists in the wax in the free state, and may also be dissolved out from it by alcohol. By treating this alcohol in the fused state (at 120°–135°) with *phosphorus* and *iodine*, it was converted into an iodide, $C^{30}H^{61}I$ or $C^{31}H^{63}I$, insoluble in ether and melting at 67°; and another substance melting at 70°–75°, which was dissolved by the ether. With *phosphorus pentachloride* it yielded a chlorinated substance probably consisting of a mixture of the compounds $C^{30}H^{61}Cl$ and $C^{30}H^{60}Cl^{2}$ or $C^{31}H^{63}Cl$ and $C^{31}H^{62}Cl^{2}$. Heated with *sulphuric acid* and then saturated with alcoholic potash, it yielded a potassium salt agreeing with the formula $C^{31}H^{63}KSO^{4}$ more nearly than with $C^{30}H^{61}KSO^{4}$.

The wax also contains small quantities of other alcohols, very difficult to separate. By repeated crystallisation from benzol and ether, it appears to yield an alcohol $C^{23}H^{48}O$, melting at 78°, and a substance $C^{38}H^{82}O^{2}$, melting at 105°.

Lastly, the wax contains a mixture of several acids differing in their melting points, but very difficult to separate from a resinous body which adheres to them.

Carnaūba or *Carnahuba wax*, which coats the leaves of *Corypha cerifera* (i. 805), also a Brazilian tree, is probably the same as Canaüba wax, inasmuch as it melts at about 84° and yields by saponification an alcohol melting at 88°. According to Bérard (*Zeitschr. f. Chem.* [2] iv. 415°), it also contains cerotic acid, which may be dissolved out by alcohol.

CANNABENE. See the next article.

CANNABIS. When Indian hemp (*Cannabis indica*) is distilled in considerable quantity with an equal weight of water, an oil lighter than water is obtained, which at 12° deposits small crystals, and is therefore a mixture of two substances, one liquid, the other solid. The liquid portion, cannabene, is colourless; has a powerful odour; boils between 235° and 240°; distils in a vacuum between 90 and 95°; gives by analysis numbers agreeing with the formula $C^{9}H^{10}$, and has a vapour-density of 4·38 (calc. 3·99). When heated it appears to be partly converted into isomeric modifications which interfere with the exact determination of its boiling point and vapour-density. It dissolves with red colour in strong sulphuric acid, and is oxidised by chromic acid, yielding acetic and valerianic acids, together with other products. Cannabene exerts a powerful intoxicating action, though in this respect it is less energetic than *cannabin*, the resin of Indian hemp (i. 734). The solid substance which separates from the crude oil, as above mentioned, crystallises from alcohol in small scales having a fatty lustre and a faint odour of hemp; it contains 84·02 p. c. carbon and 15·98 hydrogen (Personne, *J. Pharm.* [3] xxxi. 46).

Oxycannabin, $C^{9}H^{6}O^{2}$, is obtained by repeatedly treating the resinous extract of Indian hemp with nitric acid of sp. gr. 1·32 to 1·42 till the whole is dissolved, then evaporating the acid liquors, washing the deposited substance with cold water, and crystallising it from hot methylated spirit. It forms long, flat, white or slightly yellow prisms, tasteless, insoluble in water, slightly soluble in alcohol, soluble also in benzol and in chloroform, insoluble in carbon bisulphide and in ether. It dissolves in hot nitric acid and separates unchanged on evaporation; also in oil of vitriol, the solution blackening when heated. It is not altered by boiling with moderately strong potash, soda, or ammonia; its alcoholic solution is neutral to test-paper. Heated on platinum-foil it melts and burns; heated in a tube it melts at 175°–176°, and at a higher temperature sublimes without residue in long asbestos-like needles.

The acid mother-liquors of oxycannabin left, on further evaporation, an acid substance crystallising in plates (Bolas a. Francis, *Chem. Soc. J.* [2] vii. 417).

CANTHARIDIN. According to Ferrer (*Jahresb.* 1863, p. 597), this substance exists in all parts of cantharides, but most abundantly in the soft parts. From 20 grms. of *Mylabris pustulata* he obtained 0·066 grm. cantharidin; from other species of Mylabris, smaller quantities.

Mortreux (*J. Pharm.* [3] xlvi. 33) prepares cantharidin by exhausting pulverised cantharides with chloroform (or ether) and treating the evaporated extract with carbon bisulphide, which dissolves the admixed fat, and leaves nearly pure cantharidin, to be finally purified by recrystallisation from alcohol. By the use of a suitable displacement apparatus, the same process may be applied to the quantitative estimation of cantharidin. According to Mortreux's experiments, cantharides contain on the average 0·5 p. c. of cantharidin. A similar method of preparation and estimation is recommended by Fumouze (*ibid.* [4] vi. 161). According to Werner (*Jahresb.* 1867, p. 736), a quantity of cantharidin, larger by $\frac{1}{8}$ to $\frac{1}{5}$, is obtained by treating the insects with $\frac{1}{16}$ pt. finely pulverised heavy spar and $\frac{1}{250}$ dilute sulphuric acid, then quickly drying them over calcium chloride, with addition of $\frac{1}{32}$ pt. of burnt alum, and exhausting with ether.

According to Bluhm (*Zeitschr. f. Chem.* [2] i. 675; *Jahresb.* 1865, p. 571), cantharidin exists in cantharides in two modifications, one soluble, the other insoluble, in alcohol, ether, and chloroform; but the insoluble modification may be rendered soluble by treating the pulverised cantharides with an acid, or drying them mixed with water and calcined magnesia, and treating the dried mass with dilute sulphuric acid. When cantharides are desiccated with magnesia, a crystalline compound is formed, insoluble in alcohol, ether, or chloroform, and only partially soluble in water, but still possessed of vesiccating properties. With baryta also cantharidin forms a compound sparingly soluble in water; with the alkalis, easily soluble compounds. Cantharidin does not volatilise with vapour of water or alcohol. 100 pts. of the following liquids dissolve at 18° the quantities of cantharidin stated below:

Alcohol	Carbon bisulphide	Ether	Benzol	Chloroform
0·03	0·06	0·11	0·20	1·20

For the estimation of cantharidin, 30 grms. of pulverised cantharides are mixed with water and 8 to 10 grms. of calcined magnesia, and dried over the water-bath; the residue is supersaturated with dilute sulphuric acid and shaken up with ether frequently renewed; or the mass is dried a second time and treated with ether or chloroform. The residue of the ether or chloroform extract, consisting of cantharidin, fat, and a yellow substance, is treated with carbon bisulphide to remove the fat, and with alcohol to remove the yellow substance, and the residue is weighed, the quantities of cantharidin dissolved by the carbon bisulphide and the alcohol being estimated by calculation and added to the weight. By this method Bluhm found in cantharides 0·264 p. c. cantharidin, and in *Mylabris quatuordecimpustulata* 0·486 p. c.; in *M. melanura* only a very small quantity.

Dragendorff a. Mosing (*Zeitschr. f. Chem.* [2] iii. 464; iv. 308) have obtained a number of metallic derivatives of cantharidin, mostly crystallisable and represented in composition by the formulæ $C^5H^7O^3M$ and $(C^5H^7O^3)^2M''$. The compounds with the alkali-metals separate in the crystalline form on heating cantharidin with the solution of an alkaline hydrate; those of the alkaline earth-metals and heavy metals are obtained by double decomposition with the potassium compound, as sparingly soluble mostly crystalline precipitates. These precipitates, however, are generally mixed with free cantharidin, so that their composition as determined by analysis is uncertain.

According to Dragendorff (*Zeitschr. f. Chem.* [2] iii. 187), cantharidin is not poisonous to all animals, and acts upon different animals with various degrees of intensity.

Dragendorff finds also that cantharides contain a small quantity of a volatile body which passes over in distillation with water, and exerts the same physiological action as cantharidin.

CAOUTCHOUC. W. A. Miller (*Chem. Soc. J.* [2] iii. 273) has made important observations on the alteration of caoutchouc (and of gutta-percha) by the action of air and water. Caoutchouc may be left for years in the dark, exposed to the air or under water, without much alteration, but if exposed to light and to the open air, and especially to the alternate action of air and water, it soon becomes glutinous, less elastic, and more soluble in alcohol and dilute alkalis than unaltered caoutchouc. This change, which is due to oxidation, takes place more quickly with manufactured caoutchouc than with the less porous natural substance. The chemical nature of the change is shown by the following analyses: A, of natural caoutchouc; B, of manufactured caoutchouc; C, of the portion of A (11·8 p. c.) which was dissolved out by alcohol, after the caoutchouc had been exposed for nine months to air and light:

	Carbon	Hydrogen	Oxygen		
A . .	85·82	11·11	3·07	=	100
B . .	85·53	12·06	2·41	=	100
C . .	67·23	9·54	23·23	=	100

A similar result was obtained by Spiller (*ibid.* 44) in a waterproof packing-cloth consisting of cotton and dissolved caoutchouc, which had been exposed to the air for six years.

Caoutchouc swells up and dissolves with great facility in melting naphthalene (Kletzinsky, *Zeitschr. f. Chem.* [2] ii. 127).

CAPILLARITY. According to Musculus (*Chem. Centr.* 1864, p. 922; *Jahresb.* 1864, p. 5), many substances, even in small quantity, exert a considerable influence on the capillarity of water, whereas others do not perceptibly alter it. To the class of substances active in this respect belong alcohol, acetic acid, the derivatives of alcohol which are soluble in water, also the biliary acids, and soap; to the inactive class belong mineral acids, most salts, sugar, extractive matters, and albumin. Musculus estimates the force of capillarity by measuring, by means of a simple apparatus, the pressure required to expel the column of liquid from the capillary tube. He recommends capillarimetry as a delicate analytical method for the detection of substances which are active in the sense above mentioned, and especially for estimating the amount of alcohol or acetic acid in aqueous solutions. The capillarity of water being taken as unity, the following values have been obtained for other liquids, all estimated in the same capillary tube:

	Capillarity
Water	1·000
Alcohol	0·312
Acetic acid	0·393
Water containing 2 p. c. Alcohol	0·904
„ 5 p. c. „	0·800
„ 2 p. c. Acetic acid	0·950
„ 5 p. c. „	0·845

On this principle an alcoholometer called a 'liquometer' has been constructed. Its essential part consists of a graduated capillary tube about 4 inches long, and having its lower end in contact with the liquid to be tested. The point of the tube at which the liquid column finally rests indicates the proportion of alcohol in the liquid. The indications of the instrument are limited to 20 p. c. alcohol; liquids richer in alcohol must previously be diluted with a measured quantity of water. This liquometer is applicable to the testing of pure alcoholic liquids, and probably also of light wines; but not to wines rich in sugar or to beer (*Pharm. J. Trans.* [2] ix. 171; *Jahresb.* 1867, p. 14).

Wilhelmy (*Pogg. Ann.* cxxi. 44; cxxii. 1) has determined by a peculiar process the coefficients of capillarity * of a number of organic substances, and has deduced from the results the following general conclusions respecting the dependence of this physical property upon chemical composition.

1. In substances equal in their proportions of hydrogen and oxygen, the coefficient of capillarity increases with the amount of carbon: *e.g.* alcohol C^2H^6O, and acetone C^3H^6O; ethyl acetate $C^4H^8O^2$, and methyl-benzoate $C^8H^8O^2$; amylene C^5H^{10}, and xylene C^8H^{10}.

2. In like manner, with equal amounts of hydrogen and carbon, the coefficient of capillarity increases with the amount of oxygen: *e.g.* acetone C^3H^6O, ethyl-formate $C^3H^6O^2$, and lactic acid $C^3H^6O^3$.

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* The coefficient of capillarity is the weight of liquid raised by capillary action on an immersed solid body, for the linear unit of the line of contact (1 mm.). This weight, α, is calculated by the equation

$$\alpha = \frac{\pi - P - vs}{\lambda},$$

in which P denotes the weight in air of the immersed body; π, the weight which counterpoises the same body when immersed so far that the portion v of its total volume is within the liquid; λ, the length of the contact-line between the solid body and the liquid; and s, the specific gravity of the liquid.

The above equation gives

$$\pi = P = vs + \alpha\lambda.$$

Wilhelmy regards this coefficient of capillarity α as an approximate measure of the molecular cohesion of the liquid.

3. It likewise increases with the simultaneous increase of carbon and oxygen: *e.g.* methyl alcohol CH^4O, and acetic acid $C^2H^4O^2$; ethyl alcohol C^2H^6O, and lactic acid $C^3H^6O^3$.

4. Increase in the proportion of hydrogen diminishes the coefficient of capillarity: *e.g.* benzoic aldehyde C^7H^6O, and ethyl-amyl ether $C^7H^{16}O$; salicylol $C^7H^6O^2$, and amyl acetate $C^7H^{14}O^2$.

5. By increase of oxygen and diminution of hydrogen it is increased: *e.g.* butyric acid $C^4H^8O^2$, and acetic anhydride $C^4H^6O^3$.

6. The presence of chlorine, bromine, or iodine increases the coefficient of capillarity when the amount of hydrogen is at the same time diminished, and, within certain limits, even when the amount of hydrogen is increased, or that of oxygen diminished: *e.g.* ethyl chloride C^2H^5Cl, and ethylene chloride $C^2H^4Cl^2$; ethyl-amyl ether $C^7H^{16}O$, and benzoyl chloride C^7H^5OCl; ethyl oxide $C^4H^{10}O$; ethyl chloride C^2H^5Cl, bromide, and iodide.

7. Homologous compounds have equal coefficients of capillarity.

8. Increase of oxygen raises the coefficient of capillarity, even when the substance richer in oxygen differs at the same time by $\pm nCH^2$ from the one which contains less oxygen; this however is true only for compounds of similar character. As examples in which it holds good are adduced: acetic anhydride $C^4H^6O^3$, and ethyl oxalate $C^6H^{10}O^4$; amylene C^5H^{10}, and methyl valerate $C^6H^{12}O^2$; cuminol $C^9H^{10}O$, and methyl benzoate $C^8H^8O^2$; cetylene $C^{16}H^{32}$, and acetic acid $C^2H^4O^2$. As examples of compounds in which the same law does not hold good: salicylol $C^7H^6O^2$, and methyl-salicylic acid $C^8H^8O^3$; cetylene $C^{16}H^{32}$, and amyl formate $C^6H^{12}O^2$.

9. Isomeric compounds exhibit equal coefficients of capillarity only when they are allied in chemical character.

On *electro-capillary diffusion*, see Becquerel (*Compt. rend.* lxvii. 1081; *Zeitschr. f. Chem.* [2] v. 134).

CAPROIC ACID. $C^6H^{12}O^2 = C^6H^{11}O.H.O = C^5H^{11}.CO^2H$.—This acid occurs, together with butyric and valeric acids, in the flowers of *Satyrium hircinum*, which have an odour of bugs (Chautard, *Bull. Soc. Chim.* [2] ii. 56); and, together with several of its lower homologues, in the sarcocarp of *Gingko biloba* (Béchamp, *ibid.*). It has also been found by C. Kraut (*Ann. Ch. Pharm.* ciii. 29), together with butyric acid, in the water of a brook running out of peaty soil.

Caproic acid is formed synthetically:

1. By the action of carbon dioxide on sodium-amyl (produced by treating zinc-amyl with sodium):

$$\underset{\substack{\text{Sodium}\\\text{amyl}}}{C^5H^{11}Na} + CO^2 = \underset{\text{Sodium caproate}}{C^5H^{11}.COONa}$$

(Wanklyn a. Schenk, *Chem. Soc. J.* [2] vi. 31).

2. By treating amyl hydride with carbonyl chloride, whereby caproyl chloride is produced:

$$C^5H^{12} + COCl^2 = HCl + C^6H^{11}OCl;$$

converting this chloride into ethyl caproate by the action of boiling alcohol, the ethyl caproate into barium caproate, &c. (Harnitz-Harnitzky, *Bull. Soc. Chim.* [2] iii. 363).

It is also produced in the following reactions:

3. By the action of hydriodic acid upon leucine (amidocaproic acid):

$$C^6H^{11}(NH^2)O^2 + 3HI = C^6H^{12}O^2 + NH^4I + I^2$$

(Hüfner, *Zeitschr. f. Chem.* [2] iv. 391).

4. Together with hexyl alcohol and marsh gas, by the fermentation of ethyl alcohol in contact with syntonin or washed meat, and chalk (Béchamp, *ibid.* 702):

$$7C^2H^6O = 2C^6H^{12}O^2 + 2CH^4 + 2H^2 + 3H^2O$$

and

$$7C^2H^6O = C^6H^{12}O^2 + C^6H^{14}O + 2CH^4 + 4H^2O.$$

5. In small quantity, together with butyric acid, in the fermentation of St. John's bread (the fruit of *Ceratonia siliqua*) and of starch-paste (J. Sticht, *ibid.* p. 220).

6. Together with œnanthylic and valeric acids and capronitrile, in the oxidation of diamyl by nitric acid (Schorlemmer, *ibid.* 543).

7. By oxidation of octylene hydrate (secondary octyl alcohol) with potassium dibromate and sulphuric acid (P. De Clermont, *ibid.* v. 727).

8. In the dry distillation of wood. After the watery portion of the crude distillate

has been neutralised with soda, and the greater part of the sodium acetate has crystallised out, a mother-liquor is obtained which, after concentration, yields successively the sodium salts of all the fatty acids from formic to caproic (Barré, *ibid.* 445).

Caproic acid prepared by the action of alcoholic potash on amyl cyanide (i. 743) boils at 195° under a barometric pressure of 746 mm. (Rossi, *Ann. Ch. Pharm.* cxxxiii. 176).

The primary octylic ether of caproic acid $C^6H^{11}O^2.C^8H^{17}$ is one of the constituents of the volatile oil of *Heracleum sphondylium*. The acid $C^6H^{12}O^2$, obtained from it, is an oily liquid boiling between 200° and 205°, solidifying at about −10° to a white mass; it appears to be identical with the caproic acid of natural fats, but differs in some respects from that prepared from amyl cyanide, *e.g.* in the characters of its silver salt (Zincke, *Ann. Ch. Pharm.* clii. 20).

Bromocaproic acid, $C^6H^{11}BrO^2$, produced by heating 2 pts. caproic acid and 3 pts. bromine to 140°–145° for several hours, is a liquid having a less unpleasant odour than caproic acid itself, and boiling at about 240°. It is converted by potash or moist silver oxide into leucic acid, $C^6H^{12}O^3$, and by ammonia into leucine, $C^6H^{13}NO^2$ (Cahours, *Rép. Chim. pure*, iv. 145; *Jahresb.* 1862, p. 250). See also Hüfner (*Zeitschr. f. Chem.* [2] iv. 616).

CAPROIC ALDEHYDE, $C^6H^{12}O = C^5H^{11}.COH$, produced by distilling a mixture of sodium formate and caproate, and purified by separation from its compound with sodium bisulphite, is a liquid having a pungent, but not unpleasant aromatic odour, boiling at 121° (bar. at 743 mm.), slightly soluble in water, miscible with alcohol, ether, and glacial acetic acid. It reduces ammoniacal silver nitrate; is converted by oxidation into caproic acid identical with that obtained from amyl cyanide; and when dissolved in strong acetic acid, and treated with sodium-amalgam, it is converted into primary hexyl alcohol $C^6H^{14}O$, boiling at 150° (Rossi, *loc. cit.*).

CAPRYLAMIDE, $C^8H^{15}O.H^2N$ or $C^7H^{15}.CO^2NH^2$, produced by leaving ethyl caprylate in contact with strong aqueous ammonia for three months, forms large inodorous crystalline laminæ, permanent in the air, easily soluble in alcohol and ether, melting at 110°, and boiling without decomposition at a temperature above 200°. When hydrochloric acid gas is passed into its ethereal solution, a solid mass is formed, which redissolves on continuing the passage of the gas, and the ethereal solution when evaporated leaves the crystallised hydrochloride $C^8H^{17}NO.HCl$. *Antimonic chloride* acts violently on caprylamide, but if the mixture be well cooled, no decomposition takes place, the two bodies uniting directly, and forming a compound which crystallises after a few days in large four-sided prisms. *Phosphoric anhydride* converts caprylamide into caprylonitrile, $C^8H^{15}N$ (E. Felletar, *Zeitschr. f. Chem.* [2] iv. 665).

CAPRYLIC ACID. $C^8H^{16}O^2 = C^7H^{15}.CO^2H$.—This acid has been found, together with several of its homologues, in putrid yeast, in the root of *Arnica montana*, and among the products of the oxidation of Chinese wax by nitric acid (*Jahresb.* 1857, pp. 303, 403; 1861, p. 752). It is also produced by oxidising primary octyl alcohol, $C^7H^{15}.CH^2OH$ (from the fruit of *Heracleum sphondylium*), with potassium dichromate and dilute sulphuric acid (Zincke, *Zeitschr. f. Chem.* [2] v. 56). The acid obtained by this last process boils at 230°–234°, and solidifies at 12°, forming a white mass like spermaceti which melts between 16° and 17°; it appears, therefore, to be identical with the caprylic acid obtained from butter and from cocoa-nut oil (i. 745). It is slightly soluble in water, and separates therefrom at low temperatures in thin laminæ. The *barium salt* $(C^8H^{15}O^2)^2Ba$ separates from a concentrated solution by evaporation or rapid cooling in thin nacreous laminæ; by slow cooling in thin flat concentrically grouped needles. The *calcium salt* $(C^8H^{15}O^2)^2Ca.H^2O$ is very much like the barium salt, but somewhat less soluble, and the needles which it forms by slow cooling are thinner, longer, and have a fine silky lustre when dry. The *silver salt* $C^8H^{15}O^2Ag$ is a white curdy precipitate, but slightly sensitive to light or heat, dissolving when boiled with a large quantity of water, but immediately separating in flocks on cooling (Zincke).

CAPRYLONITRILE or **HEPTYL CYANIDE**, $C^8H^{15}N = C^7H^{15}.CN$, obtained by heating ammonium caprylate or caprylamide with phosphoric anhydride, is a clear colourless liquid, having a highly aromatic odour, like that of cinnamon oil, and a sweetish, aromatic, slightly burning taste. Sp. gr. = 0·8201 at 13·3°. Boiling point 194°–196°. Very inflammable; burns with a bright fuliginous flame. Mixes with alcohol and ether. By boiling with alcoholic potash it is converted into ammonia and potassium caprylate (Felletan, *Zeitschr. f. Chem.* [2] iv. 665).

CAPSULÆSCIC ACID. $C^{13}H^{12}O^{8}$.—An acid obtained from the husks of the horse-chestnut. The concentrated alcoholic decoction is left to cool; the liquid expressed from the jelly which then forms is distilled in the water-bath; and the lukewarm aqueous infusion of the residue is precipitated with neutral lead acetate. The portion of the precipitate insoluble in dilute acetic acid, after repeated decomposition with hydrogen sulphide, precipitation with lead acetate, and boiling with alcohol, yields, by evaporation of the liquid filtered from the lead sulphide, colourless crystals of capsulæscic acid. This acid sublimes without decomposition and crystallises unaltered from hot dilute hydrochloric acid. Its aqueous solution is coloured dark greenish-blue by ferric chloride, and its solution in hot potash-ley reacts like an alkaline solution of gallic acid (Rochleder, *Jahresb.* 1866, p. 693).

CARAMEL. When crude caramel obtained by heating sugar to 210°-220° is dialysed through parchment-paper (iii. 716), caramelane and caramelene pass through, whilst caramelin, the component richest in carbon (i. 748), remains on the dialyser. This purified caramel (which may also be prepared from crude caramel by repeatedly precipitating the aqueous solution with alcohol, till the precipitate is no longer plastic, but pulverulent) possesses five times the colouring power of crude caramel. A solution containing 10 p. c. of it is gummy, and coagulates on standing to a jelly perfectly soluble in water, whether hot or cold; its solution dries up in a vacuum to a black shining mass, which when it retains a certain amount of water is still tough and elastic. If this caramel has been completely dried at a comparatively low temperature, it remains soluble in water even after subsequent heating to 120°; but if its solution be directly evaporated to dryness at 100°, it becomes insoluble both in hot and in cold water. Soluble purified caramel contains 54·59 p. c. carbon, agreeing with the formula $C^{24}H^{26}O^{13}$. A solution of pure caramel is tasteless and neutral; the caramel is precipitated from it by the smallest quantities of mineral acids, alkaline sulphates, sodium chloride and most other salts, and by alcohol, as a brownish-black pulverulent substance insoluble in water; the caramel in the crude product of the roasting of sugar is protected from the action of these bodies by the presence of undecomposed sugar and brown substances of intermediate composition. Insoluble caramel obtained as above swells up to a gelatinous mass in weak potash-solution, and dissolves therein when warmed. If the solution be then dialysed, the proportion of potash in that which remains in the dialyser rapidly diminishes to 9 p. c., and on adding acetic acid, the whole of the potash passes through, and pure caramel remains (Graham, *Chem. Soc. J.* xv. 258).

Caramelane.—According to Gélis (*Rép. Chim. pure*, iv. 410), this substance may be prepared from starch-sugar, and becomes perfectly colourless when treated with animal charcoal. It cannot be reconverted into sugar. When the sugar in the preparation of caramel has not been heated long enough, or to a sufficiently high temperature, the portion of the product soluble in alcohol contains, besides caramelane, a considerable quantity of glucosane. The latter is also colourless, and differs from caramelane in being reconvertible into sugar by the action of water or dilute acids.

Methods of preparing caramel brown are described by F. Thomson and T. Sherlock (*Chem. News*, xv. 242, 282).

CARAPIN. An uncrystallisable bitter principle obtained from the bark of *Carapa guianensis.* It is nearly related to caïl-cedrin (p. 384) and tulucunin (v. 897), and is prepared in a similar manner to those bodies, but is distinguished from the former by its inferior solubility in ether, and from the latter by not being coloured by acids (Caventou, *Jahresb.* 1861, p. 769).

CARBACETOXYLIC ACID. $C^{3}H^{4}O^{4}$ (Wichelhaus, *Ann. Ch. Pharm.* cxlv. 283).—A monobasic acid isomeric with malonic acid, produced by heating β chloropropionic acid * with excess of silver oxide:

$$C^{3}H^{5}ClO^{2} + 3Ag^{2}O = C^{3}H^{3}AgO^{4} + AgCl + 2Ag^{2} + H^{2}O.$$

The resulting solution filtered, heated with sodium-amalgam as long as silver chloride is thereby precipitated, and evaporated, yields silver carbacetoxylate, $C^{3}H^{3}AgO^{4}$, in tufts of steel-grey shining needles, which may be dried at 100° without decomposition. Carbacetoxylic acid, separated from the silver salt by hydrogen sulphide, remains on evaporation as a yellowish, easily soluble syrup, having the odour of the lower fatty acids. The barium salt crystallises in spherical nodules; the lead salt in crusts; the zinc salt in shining scales; the ammonium salt is very deliquescent.

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* The modification of this acid produced from lactyl chloride is called α chloropropionic acid; that produced by the action of PCl^{5} on glyceric acid, β chloropropionic acid. (See PROPIONIC ACID.)

Carbacetoxylic acid is converted by nascent hydrogen into glyceric acid, $C^3H^6O^4$. Heated in a sealed tube to 200° with aqueous hydriodic acid, it is reduced to pyroracemic acid, $C^3H^4O^3$, with separation of iodine.

CARBACETYLIC ACID. This name is applied to pyroracemic acid by Wichelhaus (*loc. cit.*), who represents it by the constitutional formula $CH^3—CO—COOH$, regarding it as homologous with glyoxalic acid, H—CO—COOH. He finds that it is not attacked by phosphorus pentachloride, and therefore does not contain any alcoholic hydrogen, like glycollic acid, lactic acid, &c.

CARBALLYLIC ACID. Syn. with TRICARBALLYLIC ACID (v. 879).

CARBAMIC ACID. $CO^2NH^3 = NH^2.COOH$.—The ammonium salt of this acid, $CO^2.2NH^3 = NH^2.COONH^4$, is produced by the direct combination of gaseous ammonia and carbon dioxide, and by distilling ammonium sulphamate with sodium carbonate (i. 750). It is also contained in commercial carbonate of ammonia. Kolbe a. Basaroff (*Chem. Soc. J.* [2] vi. 194) prepare it by passing carbon dioxide and ammonia gases, both perfectly dry, into cold absolute alcohol, separating the copious crystalline precipitate by filtration from the greater part of the liquid, and heating it with absolute alcohol to 100° or above in a sealed tube; the liquid on cooling deposits the carbamate in large crystalline laminæ. Divers (*ibid.* viii. 215) prepares this salt by the following processes, depending partly on the direct combination of CO^2 and NH^3, partly on the dehydration of the carbonate: α. By passing carbon dioxide and ammonia gas into strong aqueous ammonia.—β. By digesting the commercial carbonate or any other carbonate of ammonia to 20°–25° in a closed vessel for 36 to 40 hours with aqueous ammonia saturated with the gas at a low temperature.—γ. By heating commercial carbonate of ammonia with anhydrous potassium carbonate to 50°–80° in a retort connected with a wide tube dipping under mercury, the carbamate then subliming in the neck.—δ. By distilling in like manner a mixture of commercial carbonate and anhydrous calcium chloride.—ε. By very slowly distilling the commercial carbonate, the more remote part of the earlier incrustation then consisting of impure carbamate.—ζ. By distilling normal ammonium carbonate at a heat not exceeding 60°.—η. By repeatedly dissolving the commercial carbonate at a gentle heat in the same quantity of water, cooling after each addition, and separating the crystals, until normal ammonium carbonate is deposited; then warming the solution; dissolving a fresh quantity of commercial carbonate in it; leaving it to cool and crystallise for a day; separating the crystals; passing ammonia gas; straining (if necessary) the precipitate of normal carbonate produced; renewing or continuing the stream of ammonia gas till the solution (kept cool) is about saturated; and straining off the precipitate of normal carbonate: the solution then exhibits the characters of the carbamate with a little carbonate dissolved in it.—θ. By distilling the commercial carbonate with strong spirit, or better, perhaps, with absolute alcohol.

Ammonium carbamate occurs in the form of flocculi; of a more or less crystalline incrustation; of prisms projecting from this incrustation; of crystalline laminæ; and of crystals neither tabular nor decidedly elongated or columnar. When exposed to moist air it gives off ammonia and is gradually converted into acid carbonate:

$$CO^2(NH^3)^2 + H^2O = NH^3 + CO^3(NH^4)H.$$

It differs from the carbonates in not melting when heated. When vaporised at any temperature, it is resolved into ammonia and carbon dioxide; but when heated in sealed tubes to 130°–140°, it is converted into urea, $[CO^2(NH^3)^2 - H^2O = CON^2H^4]$, which is therefore the amide of carbamic acid (Kolbe a. Basaroff). See UREA. It dissolves, with fall of temperature, in about 1½ pt. of water, at first without change, but after a short time it takes up water and is converted into carbonate: $CO^2(NH^3)^2 + H^2O = CO^3(NH^4)^2$.

Ammonium carbamate dissolves in spirit of sp. gr. 0·829 (J. Davy), also in absolute alcohol when heated with it in a sealed tube, and crystallises out on cooling (Kolbe a. Basaroff). It dissolves freely in strong aqueous ammonia, with production of cold. The solution, left to itself for some time, deposits crystals of the normal carbonate; but if cooled to about 0° soon after it is made, it yields the carbamate again in relatively large crystals. Ammonia, therefore, has the power of impeding the hydration of the carbamate; and this appears to be its mode of action in some of the methods above given (β, η) for preparing the carbamate from the commercial carbonate (Divers).

The distinguishing reaction between the carbamate and carbonate is that, when added *in excess* to calcium chloride and ammonia, the carbamate precipitates the calcium very slowly, whereas the carbonate precipitates it immediately. The gelatinous precipitate (calcium carbamate?) produced in solution of ammonium carbamate by excess of calcium chloride can be dissolved by sufficient water almost immediately; the gelatinous carbonate is also sensibly dissolved by water, but not nearly to the same extent as the carbamate (Divers, *Chem. Soc. J.* [2] viii. 363).

Ethyl carbamate (urethane) is formed, together with ammonium nitrate, by heating urea nitrate with absolute alcohol to 120°–130° (Baute, *Zeitschr. f. Chem.* [2] vi. 90):

$$\underset{\text{Urea nitrate.}}{CON^2H^4.HNO^3} + C^2H^5OH = NH^4.NO^3 + \underset{\text{Urethane.}}{CO(NH^2)(OC^2H^5)}$$

Benzylidene-ammonium carbamate is formed as a white solid mass when ammonium carbamate is left in contact with benzoic aldehyde over sulphuric acid:

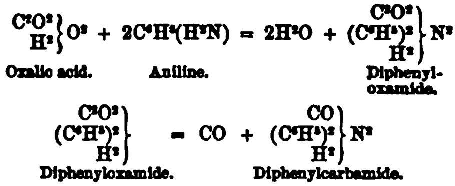
$$CO(NH^2)(ONH^4) + 2C^7H^6O = 2H^2O + CO(NH^2)[ON(C^7H^6)^2].$$

Heated with water it gives off gas; heated with alcohol it yields hydrobenzamide (E. Mulder, *Zeitschr. f. Chem.* [2] v. 58).

Ammonium Oxysulphocarbamate, $CS(NH^2)(ONH^4)$, prepared by passing gaseous carbon oxysulphide, COS, into absolute alcohol saturated with ammonia, forms crystals easily soluble in water. Its solution is precipitated by lead acetate, cupric sulphate, and uranic nitrate; by barium chloride only when heated. Hydrochloric acid added to the concentrated aqueous solution decomposes it, with evolution of gas. With *benzoic aldehyde*, the oxysulphocarbamate reacts like the carbamate, yielding the compound $CS(NH^2)[ON(C^7H^6)^2]$ (Mulder, *loc. cit.*).

CARBANILIC ACID. Reichenbach a. Beilstein (*Bull. Soc. Chim.* [2] ii. 15) have confirmed the result previously arrived at by Gerland, that Chancel's carbanilic or phenyl-carbamic acid, obtained by the action of potash on phenyl-carbamide (i. 752), is identical with amidobenzamide, not with amidodracylamide. (See BENZAMIDE, p. 257.)

CARBANILIDE, or *Diphenyl carbamide*, is formed, together with other products, by heating 1 mol. oxalic acid with 2 mol. aniline, or by the dry distillation of neutral aniline oxalate (Hofmann, *Proc. Roy. Soc.* xv. 335):



$$\underset{\text{Oxalic acid.}}{\left.\begin{matrix}C^2O^2\\H^2\end{matrix}\right\}O^2} + \underset{\text{Aniline.}}{2C^6H^5(H^2N)} = 2H^2O + \underset{\text{Diphenyl-oxamide.}}{\left.\begin{matrix}C^2O^2\\(C^6H^5)^2\\H^2\end{matrix}\right\}N^2}$$

$$\underset{\text{Diphenyloxamide.}}{\left.\begin{matrix}C^2O^2\\(C^6H^5)^2\\H^2\end{matrix}\right\}} = CO + \underset{\text{Diphenylcarbamide.}}{\left.\begin{matrix}CO\\(C^6H^5)^2\\H^2\end{matrix}\right\}N^2}$$

Diphenyl-urea, isomeric, if not identical, with carbanilide, is produced by heating 1 pt. urea to 150°–170° with 3 pts. aniline:

$$\underset{\text{Urea.}}{CN^2H^4O} + \underset{\text{Aniline.}}{2(C^6H^5)H^2N} = 2NH^3 + \underset{\text{Diphenyl-urea.}}{CN^2H^2(C^6H^5)^2O}$$

This mode of formation of diphenyl-urea is analogous to that of triphenyl-rosaniline from aniline and rosaniline (Baeyer, *Ann. Ch. Pharm.* cxxxi. 251).

CARBINOL. The generic name proposed by Kolbe for the monatomic alcohols (p. 62).

CARBINYL. The corresponding term for alcohol-radicles; *e.g.*,
Dimethyl-carbinol, $C(CH^3)^2H.OH.$
Dimethyl-carbinyl iodide, $C(CH^3)^2H.I.$

CARBODIMETHYL-DIETHYL. $C^7H^{16} = C\left\{\begin{matrix}(CH^3)^2\\(C^2H^5)^2\end{matrix}\right.$ (Friedel a. Ladenburg, *Ann. Ch. Pharm.* cxlii. 310).—A hydrocarbon of the paraffin series, produced by the action of zinc-ethyl on methyl-chloracetol (i. 27):

$$C(CH^3)^2Cl^2 + Zn(C^2H^5)^2 = ZnCl^2 + C(CH^3)^2(C^2H^5)^2.$$

To prepare methyl-chloracetol, acetone is mixed by drops with phosphorus pentachloride, cooled at the commencement of the process, and the mixture is distilled till the distillate dissolves completely in water. This distillate, washed, dried, and several times rectified, yields chloropropylene, C^3H^5Cl, between 25° and 35°, and methyl-chloracetol between 66° and 78°.

To convert this compound into carbodimethyl-diethyl, it is dropped upon zinc-ethyl contained in a flask having an upright condensing tube; and the mixture, after being warmed for some time, is distilled, the portion which goes over below 110° being collected apart. The distillate is then mixed by drops with water in a cooled flask to decompose the excess of zinc-ethyl; the zinc-oxide thereby formed is dissolved in hydrochloric acid; the oil which remains undissolved is dried and subjected to fractional distillation; and the liquid which passes over between 85° and 90° is heated for several days with sodium, to free it from still remaining chlorine. The product thus obtained is pure carbodimethyl-diethyl, boiling between 86° and 87°, having a vapour-density of 3·46 (calc. 3·62), and a sp. gr. in the liquid state of 0·7111 at 0°, and 0·6958 at 20·5°.

CARBODIPHENYL-TRIAMINE. $N^3[C^{iv}(C^6H^5)^2H^3]$.—Syn. with MELANILINE. (See PHENYLAMINES, iv. 461.)

CARBO-DODECAETHYL-TETRAPHOSPHONIUM CHLORIDE. $\left.\begin{matrix}C^{iv}\\(C^2H^5)^{12}\end{matrix}\right\}P^4Cl^4$.—Produced, together with other compounds, by the action of carbon tetrachloride on triethylphosphine (Hofmann, *Jahresb.* 1861, p. 448). See PHOSPHORUS BASES.

CARBOHYDROQUINONIC ACID. $C^7H^6O^4$.—This acid, described under DERIVATIVES OF HYDROQUINONE (iii. 214), is produced, with evolution of hydrogen, by heating quinic acid with 4 pts. potassium hydrate (Graebe, *Ann. Ch. Pharm.* cxxxviii. 197):

$$C^7H^{12}O^6 = C^7H^6O^4 + H^2 + 2H^2O.$$

It decomposes at 200°, giving off pyrocatechin and hydroquinone. The same products, but with a larger proportion of pyrocatechin, are obtained by heating carbohydroquinonic acid with mineral acids (Graebe). The isomeric acid, protocatechuic acid (iv. 738), is resolved at the same temperature into carbon dioxide and pyrocatechin without any admixture of hydroquinone. Carbohydroquinonic acid reduces a neutral silver solution at ordinary temperatures and in the dark; also cupric oxide in alkaline solution; whereas protocatechuic acid reduces silver oxide only in ammoniacal solution, and cupric oxide not at all (Hesse, *Ann. Ch. Pharm.* cxxii. 221).

CARBOMETHYL-TRIAMINE. $C^2H^7N^3 = N^3\left\{\begin{matrix}C^{iv}\\CH^3\\H^4\end{matrix}\right.$.—Syn. with METHYLURAMINE (iii. 1009).

CARBON. A variety of carbon exhibiting somewhat peculiar properties is found in small quantities at Singbhom, near Calcutta, on veins of copper and iron ore traversing clay slate. It is black, with metallic lustre, crystalline structure, and sp. gr. 1·9 (Breithaupt, *Jahresb.* 1859, p. 765).

On the spectrum of carbon, see SPECTRAL ANALYSIS (v. 389).

Carbon is, under certain circumstances, separated from cyanides in the form of graphite. The mother-liquors of the soda manufacture, which are often used for the preparation of caustic soda, are mixed with sodium nitrate, and evaporated down in iron pans for the purpose of oxidising the sulphides and cyanides (chiefly sodium ferrocyanide) contained in them. As soon as the mass has attained a dull red heat, a regular evolution of gas sets in, ferric oxide is deposited, and the surface of the liquid becomes covered with a shining layer of graphite. The separation of the graphite takes place most abundantly when the sodium nitrate is at first added only in quantity sufficient to oxidise the sulphur-compounds, and the further quantity required to decompose the cyanides is added just as the mass begins to exhibit a red heat (Pauli, *Phil. Mag.* [4] xxi. 541).

In connection with the question of the volatility of carbon at high temperatures, Elsner (*J. pr. Chem.* xcix. 257) has observed that when porcelain vessels, &c., are heated in the pottery-furnace on trays made of a mixture of clay and graphite, they become brown-black throughout their mass, and covered with a light grey specular glaze. This result is attributed by Elsner to volatilisation of the carbon. Regnault, on the other hand, ascribes it to the formation of a hydrocarbon (*Jahresb.* 1866, pp. 22, 35).

Respecting the absorptive power of charcoal for gases and vapours, see GASES.

CARBON BROMIDES. The *dibromide* C^2Br^4 is described in vol. i. p. 764; the *tribromide* C^2Br^6, or *tetrabromethylene dibromide* $C^2Br^4.Br^2$, in vol. ii. p. 571.

The *tetrabromide* CBr^4 is produced by the action of bromine, in presence of iodine bromide or antimony tribromide, on carbon bisulphide, bromopicrin, or bromoform. It is a white substance crystallising in shining plates, melting at 91°; has an ethereal odour like that of the tetrachloride, and a sweetish taste; is almost insoluble in water, but very easily soluble in ether, carbon bisulphide, carbon tetrachloride, chloroform, bromoform, benzol, and American petroleum; also in hot alcohol, from which it separates in the crystalline form on cooling. When heated in alcoholic solution it is decomposed, with formation of aldehyde and hydrobromic acid. The alcoholic solution burns with a pale green flame. The compound is rapidly decomposed by alcoholic potash or soda; thus:

$$CBr^4 + 3C^2H^5NaO + 3NaHO = 4NaBr + Na^2CO^3 + 3C^2H^6O.$$

Aqueous potash or soda does not affect it at ordinary temperatures, and only slowly at 100°, but at 150° the action goes on rapidly, the products being sodium bromide, sodium carbonate, and water. When carefully heated it sublimes unchanged, but its vapour when passed through a red-hot tube is for the most part resolved into bromine and carbon, a small quantity of a crystalline substance being however obtained, apparently consisting of the tribromide C^2Br^6 (ii. 571). By water and sodium-amalgam it is reduced, first to bromoform, $CHBr^3$, and afterwards to methylene dibromide, CH^2Br^2 (Bolas a. Groves, *Chem. Soc. J.* [2] viii. 161).

CARBON CHLORIDES. The *tetrachloride* CCl^4, heated to 200° in sealed tubes with dry *zinc oxide*, is converted into carbon oxychloride and carbon dioxide:

$$2CCl^4 + 3ZnO = 3ZnCl^2 + COCl^2 + CO^2.$$

When passed, together with *carbon dioxide*, over pumice heated to 350°, it is converted into carbon oxychloride: $CCl^4 + CO^2 = 2COCl^2$. With *carbon monoxide*, in like manner, it yields carbon oxychloride and carbon dichloride: $2CCl^4 + 2CO = 2COCl^2 + C^2Cl^4$ (Schützenberger, *Compt. rend.* lxvi. 747).

The tetrachloride heated to 100° with *sulphuric anhydride* gives off carbon oxychloride, and leaves a fuming liquid, which when distilled gives off the excess of tetrachloride at 75°, and at 130° the compound $S^2O^5Cl^2$ identical with that which Rose obtained by the action of sulphuric anhydride on brown chloride of sulphur (v. 535). The reaction is:

$$CCl^4 + 2SO^3 = S^2O^5Cl^2 + COCl^2.$$

When a mixture of sulphuric anhydride and carbon tetrachloride is heated to 100° with benzene, and the product is treated with water, hydrochloric acid, sulphobenzide, and benzene-sulphuric acid are obtained, together with a considerable quantity of benzoic acid (Schützenberger, *ibid.* lxix. 352; *Zeitschr. f. Chem.* [2] v. 631). See BENZOIC ACID, p. 306.

The *trichloride* C^2Cl^6 is formed, together with other products, when the vapour of the tetrachloride is passed through a long tube heated to moderate redness. A liquid then condenses in the receiver, coloured yellow by free chlorine and consisting of the trichloride C^2Cl^6, the dichloride C^2Cl^4, a little unaltered CCl^4, and a very small quantity of C^6Cl^6. On exposing it to light, so that the dichloride may absorb the free chlorine, and distilling till the temperature rises to 150°–160°, a residue is left in the retort consisting almost wholly of trichloride, which may be completely purified by crystallisation or by distillation with water. The distillate obtained below 160° contains a considerable quantity of dichloride, which may be converted into trichloride by the action of chlorine in sunshine (Bassett, *Chem. News*, xx. 175).

Carbon trichloride is also formed by passing chlorine into *butyric acid* heated first to 100°, afterwards to the boiling point of the acid: it then collects as a white sublimate in the neck of the retort (A. Naumann, *Ann. Ch. Pharm.* cxix. 120). According to Paterno (*Zeitschr. f. Chem.* [2] v. 246), it appears to be formed by the action of phosphorus pentachloride on acetyl chloride.

The *dichloride*, C^2Cl^4, unites with nitrogen tetroxide, forming the compound $C^2Cl^4(NO^2)^2$, which may also be regarded as *tetrachlorethylene dinitrylide*, carbon *nitrotrichloride* or *dinitro-tetrachlorethane*. This compound is formed when the dichloride is heated to 100°–120° in a sealed tube with liquid nitrogen tetroxide. The product is however somewhat scanty, as a considerable portion suffers further decomposition, resulting in the formation of carbon oxychloride. The compound $C^2Cl^4(NO^2)^2$ is a volatile crystalline compound having very much the aspect of carbon trichloride, and a rather strong odour like that of chloropicrin. It is insoluble in water, easily soluble in ether and hot alcohol, cannot be fused, but decomposes at 140° into C^2Cl^4 and NO^2.

After drying over sulphuric acid, it is somewhat glutinous, and therefore cannot be pulverised. It would probably be converted by reducing agents into a diamine (Kolbe, *Zeitschr. f. Chem.* [2] v. 430).

Julin's Chloride of Carbon, C^2Cl^2 (i. 768), is identical with hexchlorobenzene, C^6Cl^6. (See Benzene, p. 267.)

CARBON OXIDES. I. Monoxide or Carbonous oxide, CO, commonly called *Carbonic oxide*.—This gas is easily obtained pure and in large quantity by passing the gaseous mixture evolved by heating oxalic acid with sulphuric acid, first through a red-hot tube filled with charcoal, then through a mixture of potash and lime-water to absorb the small quantity of carbon dioxide still remaining undecomposed (Chevrier, *Compt. rend.* lxix. 138). It is formed in small quantity when oxygen is absorbed by an alkaline solution of pyrogallic acid, 100 vol. pure oxygen yielding about 3·5 vol. CO. When, however, the oxygen is mixed with excess of nitrogen, as in atmospheric air, the quantity of carbon monoxide thus formed is but small, and scarcely sufficient to affect the result of an eudiometrical determination (Calvert, *Chem. News*, viii. 272; Cloez, *Compt. rend.* lvii. 875; Boussingault, *ibid.* 885).

Carbon monoxide in the dry state is not decomposed by a succession of induction-sparks or by a spiral of iron or platinum wire intensely ignited by the electric current; but over water it is decomposed by the glowing platinum spiral, the carbon monoxide being converted into dioxide and replaced by an equal volume of hydrogen (Buff a. Hofmann, *Chem. Soc. J.* xii. 273).

Respecting the decomposition of carbon monoxide by heat, see Chemical Affinity and Dissociation. On the temperature of its flame and the results of its combustion under pressure, see Combustion.

Carbon monoxide passed over heated *sodamide* converts it into sodium cyanide: $NaH^2N + CO = NaCN + H^2O$, ammonia and sodium hydrate being also formed as secondary products by the action of the water on the sodamide (Beilstein a. Geuther, *Ann. Ch. Pharm.* cviii. 88).

With *sodium-ethyl*, carbon monoxide forms propione or diethyl-ketone; thus:

$$CO + 2NaC^2H^5 = CO(C^2H^5)^2 + Na^2.$$

This reaction is general:

$$CO + 2NaC^nH^{n+1} = CO(C^nH^{2n+1})^2 + Na^2$$

(Wanklyn, *Chem. Soc. J.* [2] iv. 13, 326).

With *potassium*, carbon monoxide unites directly, at about 80°, forming the compound $K^2C^2O^2$ (iv. 696). Also with *sulphur*, forming carbon oxysulphide, COS (p. 407).

When a mixture of carbon monoxide and *chlorine* is passed over *platinum sponge* heated to 400°, carbon oxychloride is formed, together with a crystallisable compound of carbon monoxide with platinic chloride, $(CO)^2PtCl^4$ (Schützenberger, *Zeitschr. f. Chem.* [2] iv. 321). See Platinum.

A mixture of carbon monoxide and carbon *tetrachloride* passed over heated pumice yields phosgene and carbon dichloride (p. 400).

For the reaction of carbon monoxide with *blood*, see p. 354.

Carbon Dioxide, Carbonic Anhydride, or Carbanhydride, CO^2, commonly called *Carbonic acid*.—This gas may be liquefied under the ordinary atmospheric pressure by a temperature of −87°, produced by evaporating liquefied ammonia over sulphuric acid in a vacuum. At the same temperature, under a pressure of three or four atmospheres, the carbon dioxide solidifies to a mass which has the transparency of ice, and may be divided, by pressure with a glass rod, into cubic crystals three or four millim. thick; these crystals are unctuous to the touch, and burn severely when pressed between the fingers. Mixed with ether in a crucible, they produce a cold of −81° (Loir a. Drion, *Compt. rend.* lii. 748; *Jahresb.* 1860, p. 42; 1861, p. 109).

Liquid carbon dioxide boils at −78·2° under a pressure of 760 mm. (Regnault, *Jahresb.* 1863, p. 70). Its expansion by change of temperature is exhibited in the following table:

Temperature	Volume
−10°	0·9517
0	1·0000
+10	1·0585
20	1·1457

Its sp. gr. at 0° (compared with water at the same temperature) is 0·9470 (Andréeff, *Ann. Ch. Pharm.* cx. 1).

The following determinations of its vapour-tension at different temperatures are given by Regnault (*Rélation des Expériences*, &c.; *Jahresb.* 1863, p. 66):

Temp.	Tension in millim. of Mercury.	Temp.	Tension in millim. of Mercury.
−25°	13007·02	+15°	39646·86
−20	15142·44	+20	44716·58
−15	17582·48	+25	50207·32
−10	20340·20	+30	56119·05
−5	23441·34	+35	62447·30
0	26906·60	+40	69184·45
+5	30753·80	+45	76314·60
+10	34998·65		

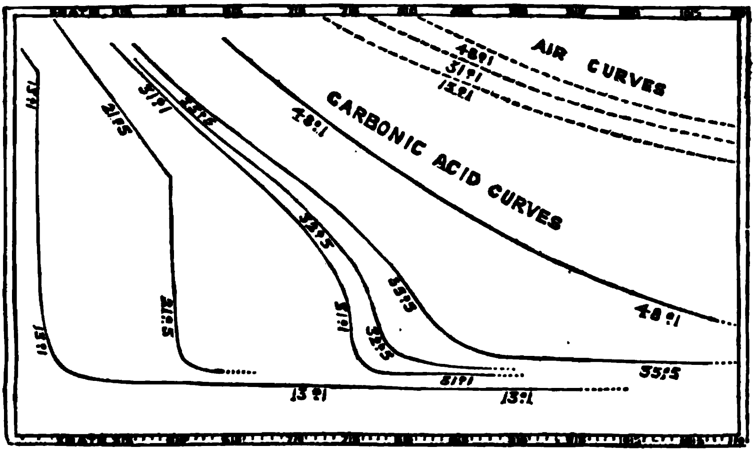
Gore (*Chem. Soc. J.* xv. 163) has described a method by which small quantities of liquid carbon dioxide may be safely prepared in stout glass tubes closed with gutta-percha stoppers, and solid substances attached to the stoppers submitted to its action. Having in this way examined its action on more than fifty substances, he concludes that it is comparatively an inactive substance, and is not deoxidised by any ordinary reducing agent except the alkali-metals. Its solvent powers are also very limited. It dissolves camphor, iodine sparingly, and a few other substances in small quantity; it does not dissolve any oxygen-salt, and does not redden extract of litmus. It abstracts the colouring matter of gutta-percha. Caoutchouc left in contact with it for some time, swells up strongly after removal, then slowly contracts again and appears white. The liquid anhydride is a bad conductor of electricity. In its general properties it is somewhat analogous to carbon bisulphide, but has much less power of dissolving fatty bodies.

At the temperature of 0°, gaseous carbon dioxide is reduced to the liquid state under a pressure of thirty-six atmospheres; as the temperature rises, greater pressure is required to effect the liquefaction, and above a certain temperature the gas is no longer liquefied by pressure. The effect of pressure on carbon dioxide at various temperatures has lately been very carefully investigated by Dr. Andrews (*Phil. Trans.* 1869, p. 575; *Chem. Soc. J.* [2] viii. 74; abstr. *Proc. Roy. Soc.* xviii. 42). When this gas is partially liquefied by pressure, and the temperature is gradually raised to about 31°, the surface of demarcation between the liquid and the gas becomes fainter, loses its curvature, and at last disappears, the tube being then filled with a fluid which, from its optical and other properties, appears to be perfectly homogeneous, the phenomena being in fact similar to those observed by Cagniard de la Tour on heating water, alcohol, ether, or petroleum in sealed tubes (HEAT, iii. 95). The temperature at which carbon dioxide ceases to be liquefied by pressure is designated by Andrews as the 'critical point,' and he finds it to be 30·92°. At temperatures a little above this point, although no liquefaction occurs, a very great change of density is produced by slight alterations of pressure, and the flickering movements above mentioned come conspicuously into view.

At 13·1°, under a pressure of 48·9 atmospheres, the gas, then just on the point of liquefying, is reduced to $\frac{1}{80\cdot5}$ of the volume it occupied under one atmosphere. After liquefaction, the volume of the gas, already reduced to $\frac{1}{470}$ of its original volume, continues to diminish as the pressure augments, and at a much greater rate than in ordinary liquids. Similar results were obtained at 21·5°. At 31·1°, or 0·2° above the critical point, the volume of the gas diminished steadily with the pressure, till about 74 atmospheres were attained. After this a rapid fall occurred (but not abrupt, as in the case of liquefaction), and the volume was diminished to one-half by an additional pressure of less than two atmospheres. Under a pressure of 75·4 atmospheres the gas was reduced to $\frac{1}{311}$ of its volume under one atmosphere. Beyond this point it yielded very slowly to pressure. During the stage of rapid contraction there was no evidence at any time of liquefaction having occurred, or of two conditions of matter being present in the tube. At 32·5° and 35·5° the same general results were observed, except that the rapid diminution of volume became less marked as the temperature was higher. The experiments at 35·5° were carried as far as 107 atmospheres, at which pressure the volume of the gas was almost the same as that which it would have occupied if it had been derived directly from liquid carbon dioxide according to the law of the expansion of that body for heat. Lastly, at 48·1°, between the pressure of 62·6 and 109·4 atmospheres, the rapid fall exhibited at lower temperatures almost if not wholly disappears, and the curve representing the changes of volume approximates closely to that of a gas following the law of Mariotte, though the actual diminution of volume is much greater than if that law held good.

These results are represented graphically by the curves in fig. 10. Equal volumes of air and carbon dioxide, measured at 0° and 760 mm., when compressed at the temperatures marked on each curve, undergo the changes of volume indicated by the form of the curve. The figures at the top and bottom indicate the approximate pressures in atmospheres; the volumes of the gas and air are measured upwards from the dotted horizontal line.

FIG. 10.



Under pressures still higher than those above mentioned, carbon dioxide may also be made to pass, without break or interruption, from what is universally regarded as the gaseous to what is in like manner universally regarded as the liquid state of matter. Thus, if a given volume of the gas at 50° or a higher temperature be exposed to a pressure increasing up to 150 atmospheres, its volume will steadily diminish as the pressure increases, and no sudden diminution of volume, without the application of external pressure, will occur at any stage of the process. When the full pressure has been applied, let the gas be allowed to cool down to the ordinary temperature of the atmosphere. During the whole of this operation no breach of continuity will occur. It begins with a gas, and by a series of gradual changes, nowhere presenting any abrupt alteration of volume or sudden evolution of heat, it ends with a liquid. The closest observation indeed fails to discover anywhere indications of a change of condition in the carbon dioxide, or evidence, at any stage of the process, of part of the compound being in one physical state and part in another. That the gas is actually changed to a liquid would indeed never have been suspected, did it not show itself to be so changed by entering into ebullition on the removal of the pressure.

From all these results, it may be inferred that the ordinary gaseous and ordinary liquid states are only widely separated forms of the same condition of matter, and may be made to pass into one another by a series of gradations so gentle that the passage shall nowhere present any interruption or breach of continuity. From carbon dioxide as a perfect gas to carbon dioxide as a perfect liquid, the transition may be accomplished by a continuous process, and the gas and liquid are only distant stages of a long series of continuous physical changes. Under certain conditions of temperature and pressure indeed, carbon dioxide finds itself in what may be described as a state of instability, and suddenly passes, with evolution of heat, and without application of additional pressure or change of temperature, to the volume, which by the continuous process can only be reached through a long and circuitous route. In the abrupt change which here occurs, a marked difference is exhibited, while the process is going on, in the optical and other physical properties of the carbon dioxide which has collapsed into the smaller volume, and of the carbon dioxide not yet altered. There is no difficulty here, therefore, in distinguishing between the liquid and the gas. But in other cases the distinction cannot be made; and under many of the conditions above described, it would be vain to attempt to assign carbon dioxide to the liquid rather than the gaseous state.

Nitrogen monoxide, hydrogen chloride, ammonia, common ether, and carbon bisulphide, all resemble carbon dioxide in exhibiting critical points when exposed under pressure to the required temperatures. Andrews proposes, instead of the present arbitrary distinction between vapours and gases, to confine the term vapour to gaseous bodies below their critical points, and therefore capable of being liquefied by pressure alone, so that gas and liquid may exist in the same vessel in presence of each other.

Reactions.—1. Gaseous carbon dioxide is slowly decomposed by the induction-spark, more quickly by the very high temperature of the electric arc (between iron terminals), into carbon monoxide and oxygen, the latter combining with the iron, and leaving a volume of carbon monoxide equal to the original volume of the gas (Buff a. Hofmann, *Chem. Soc. J.* xii. 282).—2. Respecting its decomposition by heat, see CHEMICAL AFFINITY and DISSOCIATION.—3. Mixed with *carbon tetrachloride* and passed over heated pumice, it forms carbon oxychloride: $CO^2 + CCl^4 = 2COCl^2$ (p. 400).—4. Passed over gently heated *sodamide*, it forms cyanamide and sodium hydrate: $CO^2 + 2NaH^2N = (CN)H^2N + 2NaHO$ (Beilstein a. Geuther, *Ann. Ch. Pharm.* cviii. 88).

5. With the *sodium-compounds of the alcohol radicles* C^nH^{2n+1}, it forms the sodium salts of the next higher fatty acids: *e.g.*,

$$\underset{\substack{\text{Sodium}\\\text{ethyl}}}{C^2H^5Na} + CO^2 = \underset{\substack{\text{Sodium}\\\text{propionate}}}{C^2H^5.CO^2Na}$$

(Wanklyn, *Chem. Soc. J.* xi. 103).

6. *Potassium* immersed for about twenty-four hours in an atmosphere of carbon dioxide standing over lukewarm water, is converted into a mixture of formate and acid carbonate of potassium:

$$2CO^2 + K^2 + H^2O = \underset{\text{Formate.}}{CHKO^2} + \underset{\substack{\text{Acid}\\\text{carbonate.}}}{CHKO^3}$$

Sodium acts in a similar manner, but appears to produce a smaller proportion of formate (Kolbe a. Schmidt, *Ann. Ch. Pharm.* cxix. 251).

7. *Sodium* heated with dry sand and exposed to a rapid current of dry carbon dioxide, the pasty mixture being well stirred and the temperature ultimately raised to about the boiling point of mercury, is converted into sodium oxalate:

$$2CO^2 + Na^2 = C^2Na^2O^4.$$

A similar reaction takes place with an alloy of sodium and potassium, or with potassium amalgam, the latter being heated to the boiling point; this last method seems indeed to yield the largest quantity of oxalate (Drechsel, *Zeitschr. f. Chem.* [2] iv. 120).

8. According to J. Kolb (*Compt. rend.* lxiv. 862), dry carbon dioxide is not absorbed by the anhydrous oxides or the dry hydrates of the alkali-metals or alkaline-earth metals even after prolonged contact, the presence of water being absolutely necessary to promote the absorption. This statement is, however, somewhat at variance with the well-known fact that carbon dioxide is readily taken up by ignited soda-lime. According to Beketoff (*Jahresb.* 1865, p. 14), carbon dioxide decomposes a solution of calcium acetate under a pressure of 27 or 28 atmospheres, spicular crystals of calcium carbonate being formed in the liquid; on the other hand, it does not decompose a dilute solution of calcium chloride at 45 atmospheres, of barium chloride at 40 atmospheres, or of barium acetate at 30 atmospheres.

Absorption by Water and Saline Solutions.—Khanikoff a. Louguinine (*Ann. Ch. Phys.* [4] xi. 112) have determined the quantities of carbon dioxide absorbed by water under different pressures, and have obtained results not quite in accordance with the law of Dalton a. Henry (ii. 792). In the following table α denotes the volume of carbon dioxide, reduced to 0° and 760 mm., absorbed by 1 vol. water under the pressure P:

P	α	P	α
697·71	0·9441	2188·65	3·1764
809·03	1·1619	2369·02	3·4857
1289·41	1·8647	2554·00	3·7152
1469·95	2·1623	2738·33	4·0031
2002·06	2·9076	3109·51	4·5006

Denoting two of these absorption-coefficients by α^1 and $\alpha^1 + n$, and the corresponding pressures by P^1 and P^{1+n}, the law of Henry a. Dalton would give $\frac{\alpha^1 + n}{\alpha^1} - \frac{P^1 + n}{P^1} = 0$; but on calculating the differences of these quotients from the preceding table, the terms of the resulting series exhibit, with increasing pressure, an augmentation regular enough to show that the deviation from the law above mentioned cannot be attributed to errors of experiment.

When water is saturated with carbon dioxide under pressure (as in making soda-water), the force with which the gas is retained depends to a considerable extent on the time during which the gas and water have been kept in contact and agitated together. If the agitation be continued merely for an hour or an hour and a half, then, on letting out the water, the excess of carbonic anhydride is immediately disengaged with effervescence throughout the whole mass of the liquid, which becomes creamy; whereas if the gas be left in contact with the water in the closed vessel for 20 to 24 hours, and the liquid be then let out, the carbonic anhydride disengages itself from the water and attaches itself to the sides of the glass. It appears indeed as if after a short contact the carbonic anhydride dissolves in the water as such, but that after prolonged contact it becomes hydrated and dissolves as hydrogen carbonate or carbonic acid, and is then retained more firmly. The dissolution of the carbonic anhydride is greatly accelerated by adding a little common salt to the water, the acceleration being probably due to a reaction between the sodium chloride and carbonic acid, resulting in the formation of acid sodium carbonate and hydrochloric acid. The presence of the latter acid in the resulting solution may in fact be demonstrated by means of ultramarine, which is acted upon by hydrochloric acid, but not by sodium chloride. A solution of lead chloride is acted upon in a similar manner by carbonic acid, a precipitate being gradually formed consisting of carbonate-chloride of lead (Hugo Müller, *Chem. Soc. J.* [2] viii. 37). A solution of ordinary *sodium phosphate* into which carbonic anhydride is passed is partly decomposed in like manner, with formation of acid phosphate and acid carbonate of sodium. Respecting the law of absorption of carbonic anhydride by aqueous sodium phosphate, see Heidenhain a. Meyer, *Ann. Ch. Pharm. Suppl.* ii. 157; *Jahresb.* 1863, p. 92.

CARBON OXYBROMIDE, $COBr^2$, is formed when a mixture of bromine-vapour and carbon monoxide, the latter in excess, is exposed to the sun's rays. The mixture becomes nearly colourless, and on bringing it in contact with potash-ley, rapid absorption takes place, the solution containing bromide and carbonate of potassium (J. Schiel, *Ann. Ch. Pharm. Suppl.* ii. 311; *Jahresb.* 1863, p. 155).

CARBON OXYCHLORIDE. $COCl^2$. *Carbonyl chloride. Phosgene.*—The following is given by Wilm a. Wischin (*Zeitschr. f. Chem.* [2] iv. 5) as the best method of obtaining considerable quantities of this gas, free from chlorine and containing only a *slight* excess of carbon monoxide. Into a 10-litre flask of white glass, exposed to sunshine and fitted with a caoutchouc stopper traversed by three tubes, carbon monoxide (prepared from oxalic acid, purified by passing through a mixture of potash and lime, and dried by oil of vitriol) is admitted on one side, and dry chlorine on the other, the two gases being directed on to the bottom of the flask, the carbon monoxide at a slightly more rapid rate than the chlorine, whereby a perfect mixture is effected almost instantaneously. The gaseous mixture is then directed through the third tube to the bottom of a second flask of the same size, the stopper of which is traversed by two tubes, and from this it passes into a third flask fitted up in a similar manner. The gas which passes into the third flask is nearly pure phosgene, quite free from chlorine, and containing only a slight excess of carbon monoxide. By passing it into well-cooled absolute alcohol, it is easy in favourable weather to prepare 2 or 3 pounds of ethyl chlorocarbonate in the course of a day.

On the formation of carbon oxychloride from carbon tetrachloride, see p. 400.

Phosgene is also produced by the oxidation of chloroform with potassium dichromate and sulphuric acid:

$$2CHCl^3 + O^3 = 2COCl^2 + H^2O + Cl^2,$$

a certain quantity of carbon dioxide being formed at the same time by further decomposition. The gas is evolved slowly or quickly accordingly as the mixture is heated in the water-bath or at a higher temperature; in the latter case it also contains free oxygen. To evolve phosgene quite free from oxygen in not too slow a stream, a mixture of 50 pts. potassium dichromate, 400 strong sulphuric acid, and 20 pts. chloroform is exposed to the heat of a water-bath in a flask fitted with an inverted Liebig's condenser, so that the chloroform which distils over may flow back again. To the farther end of the condenser is attached a rather large wide U-tube filled with coarse lumps of metallic antimony, to retain the free chlorine. This tube should be slightly warmed from time to time with the flame of a spirit-lamp, to prevent it from getting stopped up by the formation of solid antimonious chloride. The phosgene gas thus evolved contains about 10 p. c. of carbon dioxide and a small quantity of chloroform-vapour, which cannot be removed by any dry absorbent (Emmerling a. Lengyel, *Ann. Ch. Pharm. Suppl.* vii. 104).

Liquid Phosgene.—The gas prepared by the method just described condenses to a liquid at 0°, or more quickly at the temperature of a mixture of ice and salt. Only a portion of it can however be thus condensed, but the remaining gas may be used for other purposes. 20 grms. chloroform decomposed as above yielded only 4 grms. of rectified liquid phosgene, whereas the theoretical quantity would be 16 grms. Moreover, the liquid phosgene thus obtained always contains chloroform.

A purer and more abundant product may be obtained by evolving the gas by Wilm a. Wischin's method above described. As, however, the presence of an uncondensable gas offers a great obstacle to the liquefaction of the phosgene, it is best to regulate the flow of the two gases, so that the chlorine may be in slight excess instead of the carbon monoxide, this excess of chlorine being removed as above by passing the gas over metallic antimony. From the antimony tube it is passed through a wide U-tube cooled by a freezing mixture, and from this the liquefied phosgene is from time to time quickly poured into a small flask also surrounded by a freezing mixture. Using stoppered bottles of the capacity of 3 or 4 litres, instead of the 10-litre flasks employed by Wilm and Wischin, and with a consumption of 80 litres of carbon monoxide, the quantity of liquid phosgene obtained in the course of a sunny day was about 110 grms.; on a cloudy day, 60 litres carbon monoxide yielded about 50 grms. of liquid phosgene.

Phosgene obtained by the method just described is perfectly pure, whereas that prepared from chloroform cannot be completely freed from the latter, even by repeated fractionation.

Pure phosgene is a limpid very mobile liquid, whose vapours exhibit in the greatest intensity the well-known suffocating odour of phosgene gas. In water it sinks in the form of an oil, and gradually decomposes, with evolution of carbon dioxide. It boils constantly at 8·2° (corr.) under a pressure of 756·4 mm. Vapour-density = 3·505 (calc. = 3·420). Sp. gr. of the liquid = 1·432 at 0°; 1·392 at 18·6°, compared with water at 4° (Emmerling a. Lengyel).

Phosgene gas is gradually absorbed by *zinc-methyl*, forming a white crystalline mass, which is decomposed by water, giving off carbon monoxide (and probably also marsh gas), and a mixture of propylic and butylic alcohols, together with a small quantity of acetic acid (Buttlerow, *Jahresb.* 1863, p. 475).

According to Berthelot (*Zeitschr. f. Chem.* [2] v. 480), phosgene does not act upon ethylene, acetylene, or benzene in the manner described by Harnitzky; the observations of other chemists, however, are in accordance with Harnitzky's results. (See BENZENE, p. 262, and BENZOIC ACID, p. 306.) With *acetone* it produces dichloracetone (Wroblevsky, *ibid.* iv. 565).

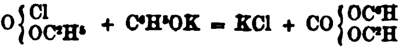
Chlorocarbonic Ethers. Ethyl-chlorocarbonate acts violently on *zinc-methyl*, producing carbon dioxide, ethylene, marsh gas (perhaps also methyl-ethyl), and zinc chloride:

$$2COCl(OC^2H^5) + Zn(CH^3)^2 = 2CO^2 + 2C^2H^4 + 2CH^4 + ZnCl^2.$$

Methyl chlorocarbonate does not act on zinc-methyl under the ordinary atmospheric pressure; and when the mixture is heated to nearly 100°, only partial decomposition takes place, resulting in the formation of methyl carbonate and hydrocarbons (ethylene and its homologues), also carbon dioxide and methyl chloride, the latter being produced by a simple splitting up of the methyl chlorocarbonate in presence of the zinc chloride produced. *Plumbotetramethyl* and *mercury-methyl* are likewise only imperfectly decomposed by methyl chlorocarbonate at 100°.

Ethyl chlorocarbonate is converted by *zinc* and *sulphuric acid* into ethyl carbonate; by *sodium-amalgam* into alcohol, sodium carbonate, and sodium chloride; by *alcohol* alone at ordinary temperatures, into ethyl carbonate and hydrochloric acid (Buttlerow, *Zeitschr Ch. Pharm.* 1863, p. 484; *Jahresb.* 1863, p. 474).

Ethyl chlorocarbonate gradually mixed with *potassium phenate* yields potassium chloride and ethyl-phenyl carbonate (Fatianoff, *Zeitschr. Ch. Pharm.* 1864, p. 77):



$$CO\left\{\begin{matrix}Cl\\OC^2H^5\end{matrix}\right. + C^6H^5OK = KCl + CO\left\{\begin{matrix}OC^6H^5\\OC^2H^5.\end{matrix}\right.$$

With *sodium monosulphide* it forms the ethylic ether of dicarbothionic acid, $S(CO^2H)^2$ (V. Meyer, *Deut. Chem. Ges. Ber.* 1869, p. 297):

$$2COCl(OC^2H^5) + Na^2S = 2NaCl + S(COOC^2H^5)^2.$$

CARBON OXYSULPHIDE. COS.—This compound, discovered by Than (*Ann. Ch. Pharm. Suppl.* v. 326), is produced: 1. By direct combination, when carbon monoxide mixed with excess of sulphur-vapour is passed through a red-hot porcelain tube. As thus prepared, however, it is always mixed with free carbon monoxide.—2. A purer product is obtained by decomposing potassium sulphocyanate with moderately dilute acids. Potassium sulphocyanate is added to a cooled mixture of 5 vol. strong sulphuric acid and 4 vol. water as long as the mass remains liquid, the action being moderated by cooling, or assisted by warming, as may be necessary; and the evolved gas—after passing through three U-tubes, the first containing cotton-wool impregnated with moist mercuric oxide to remove traces of hydrocyanic and formic acids, the second containing fine cuttings of non-vulcanised caoutchouc to absorb carbon bisulphide, and the third containing calcium chloride to absorb water—is collected over mercury. The formation of carbon oxysulphide from sulphocyanic acid is represented by the equation:

$$CSHN + H^2O = NH^3 + CSO,$$

which, however, holds good only for a fraction of the mixture, a large portion of the sulphocyanic acid being at the same time resolved into hydrocyanic and persulphocyanic acids, especially when heat is applied (iv. 379) (Than).

3. By heating urea with carbon bisulphide to 110° in a sealed tube, ammonium sulphocyanate being formed at the same time:

$$COH^4N^2 + CS^2 = COS + CSN.NH^4.$$

On opening the tube, the carbon oxysulphide is given off, together with hydrogen sulphide, from which it may be freed by lead acetate (Ladenburg, *Zeitschr. f. Chem.* [2] v. 253).

4. Together with diethyl-urea, by passing dry hydrogen sulphide into ethyl cyanate (Ladenburg, *ibid.* 345):

$$2CONC^2H^5 + H^2S = COS + COH^2(C^2H^5)^2N^2.$$

5. Thiacetic acid heated to 300° is decomposed, with evolution of a gaseous mixture, three-fourths of which consists of hydrogen sulphide, and one-fourth of carbon oxysulphide, perhaps mixed with a little methyl and marsh gas (Ladenburg, *loc. cit.*).

6. Together with sulphurous oxide, hydrochloric acid, and free sulphur, by heating equivalent quantities of chlorhydrosulphuric acid and carbon bisulphide to 100° for several hours in a sealed tube:

$$SO^2ClHO + CS^2 = COS + HCl + SO^2 + S.$$

The sulphur is deposited in large yellow crystals; the sulphurous oxide condenses to a liquid; and on opening the tube, this compound is given off as gas, together with hydrochloric acid and carbon oxysulphide, which may be freed from the other two gases by collecting it over water (Dewar a. Cranston, *Chem. News*, xx. 174).

7. Together with sulphurous oxide and free sulphur, by gently heating carbon bisulphide with an equivalent quantity of sulphuric oxide (Armstrong, *Zeitschr. f. Chem.* [2] vi. 247).

Carbon oxysulphide is a gas of sp. gr. 2·1046 (calc. 2·0833), and may easily be poured from one vessel to another. It has an aromatic odour like that of some resins, slightly also that of hydrogen sulphide, and a feebler acid reaction than carbon dioxide. At a low red heat it is partly resolved into carbon monoxide and sulphur-vapour; by a fine platinum wire ignited by the electric current, it is slowly but completely decomposed, yielding an equal volume of carbon monoxide. It burns in the air with a faint blue flame, producing carbon dioxide and sulphur dioxide; with 1½ vol. oxygen, it forms an explosive mixture burning with a shining bluish-white flame. It is not acted upon by chlorine or fuming nitric acid at ordinary temperatures, and does not form an explosive mixture with nitrogen dioxide (Than).

Water absorbs about its own volume of carbon oxysulphide, acquiring a sweetish and afterwards a pungent taste, and decomposing it after some time. It appears to exist in some sulphur springs and in the sulphurous gases of volcanos. *Potash-ley* absorbs the gas as completely as carbon dioxide, though less quickly; the solution exhibits the reactions of metallic sulphides, and when treated with acids gives off H^2S and CO^2:

$$COS + 4KHO = CO^3K^2 + K^2S + 2H^2O.$$

Baryta and *lime water* act in a similar manner (Than). It is absorbed by alcoholic potash-solution cooled to a very low temperature, the liquid ultimately solidifying to a crystalline mass of the potassium salt of ethyl-dioxysulphocarbonic acid (v. 49): $COS + C^2H^5OK = CSO^2(C^2H^5)K$ (Bender, *Zeitschr. f. Chem.* [2] v. 302).

Neutral or acid solutions of *lead*, *copper*, *cadmium*, and *silver salts* are not precipitated by the gas; but when mixed with excess of ammonia, they yield with it characteristic precipitates of metallic sulphides. *Mercury* is not altered by the dry gas at ordinary temperatures, but at the boiling heat it slowly becomes covered with a film of mercuric sulphide; the moist gas produces this effect at ordinary temperatures. *Sodium* decomposes it even in the cold, and at a low red heat burns in it with explosion, forming a black substance. Finely divided *copper*, *silver*, and *iron* decompose it without separation of free sulphur. *Mercuric ethide*, heated to boiling in a stream of the gas, is violently decomposed, yielding metallic mercury and a yellowish liquid (probably ethyl thiopropionate) having an alliaceous odour (Than).

Carbon oxysulphide unites quickly with dry *ammonia gas*, and is rapidly absorbed by strong aqueous ammonia, forming oxysulphocarbamate: $COS + 2NH^3 = CH^3NSO.NH^3$, which when dissolved in water and heated in a sealed tube, is converted into ammonium sulphocyanate: $CH^3NSO.NH^3 - H^2O = CHNS.NH^3$, and when gently heated with a lead-compound, is converted into urea, $CH^3NSO.NH^3 - H^2S = CH^4N^2O$. The reaction with ammonia affords a ready means of distinguishing carbon oxysulphide from the bisulphide, which is but slowly acted upon by ammonia (Berthelot, *Zeitschr. f. Chem.* [2] iv. 415). According to Hofmann (*ibid.* v. 345), the best reagent for separating the two compounds is *triethylphosphine*, which unites immediately with the bisulphide, but has no action on the oxysulphide.

CARBON SELENIDE. CSe^2.—Formed, but in very small quantity, when moist vapour of carbon tetrachloride is passed over phosphorus selenide. The hydrogen selenide formed by the action of the water on the phosphorus selenide then reacts with the carbon chloride as follows:

$$CCl^4 + 2H^2Se = 4HCl + CSe^2.$$

It has not been obtained pure, but appears to be a liquid having an intensely pungent and tear-exciting odour, resembling also when diluted that of carbon bisulphide. With alcoholic potash it yields the ethylic ether of selenioxanthic acid, $C^5H^{10}SeO^2$ (Rathke, *Zeitschr. f. Chem.* [2] v. 722).

CARBON SULPHIDES. I. BISULPHIDE. CS^2.—This compound is now prepared on a very large scale and applied to a variety of purposes. The several forms of apparatus used for its manufacture are similar in principle to the laboratory apparatus already described (i. 776), differing only in the forms of the retort and condenser, and in the mode of introducing the sulphur. For descriptions and figures see Richardson and Watts's *Chemical Technology*, pt. iii. pp. 124–130. According to Sidot (*Compt. rend.* lxix. 1303), the largest product is obtained at a red heat (not above that temperature). Wagner has suggested the production of carbon bisulphide by distilling some of the metallic sulphides with charcoal in closed vessels.

To purify carbon bisulphide obtained as above from free sulphur, hydrogen sulphide, and small quantities of other sulphur-compounds which give it an intensely disgusting odour, it must be rectified and treated with absorbents. Bonière uses for this purpose a series of water-bath stills, the first containing potash-ley, and the others solutions of lead, copper, iron, &c., to retain the hydrogen-sulphide, &c. (Wagner's *Jahresbericht*, 1860. p. 76). Sidot (*loc. cit.*) first distils it alone, and then agitates it with mercury till the shining surface of the metal is no longer blackened by it. Cloez (*Compt. rend.* lxix. 1356) leaves it in contact for 24 hours, and frequently agitates it, with ½ p. c. of its weight of mercuric chloride, which removes a fetid sulphur-compound; then decants the clear liquid; adds 0·02 of its weight of an inodorous fat; and distils it in the water-bath at a low temperature. The bisulphide purified by either of these processes has an ethereal odour quite different from that of the ordinary commercial product.

Uses.—Carbon bisulphide is now used for a variety of industrial purposes, chiefly on account of its solvent power, *e.g.* for the vulcanisation of caoutchouc; as a solvent of caoutchouc and gutta-percha; as a substitute for ether in dissolving quinine and other alkaloïds; for the extraction of fatty matter from vegetable and animal tissues; for recovering the oils retained by the press-cake of olives and other seeds; for extracting oils and aromatic principles from seeds, spices, &c., and even for extracting the scents of flowers; for these latter purposes it must of course be very pure; also for dissolving bitumen and sulphur from certain rocks in which they exist in too small a proportion to be extracted economically by other processes.

The poisonous properties of carbon bisulphide have been turned to account for the destruction of insects. According to Doyère (*Technologiste*, Aug. 1857, p. 573), grain may be readily freed from insects, if kept in closed receptacles, with a small addition of the bisulphide (2 grams of the latter to 100 kilo. of the grain). The bisulphide not only kills the insects, but also the larvæ and ova. The odour may be completely removed by merely exposing the grain for a short time to the air.

Lastly, the bisulphide is used in electroplating, a few drops added to the liquid causing the silver to deposit with increased brightness.

For details respecting the industrial applications of the bisulphide, see *Chemical Technology*, pt. iii. pp. 134–141; also Hofmann's *Exhibition Report*, 1862, p. 93.

Reactions.—1. Carbon bisulphide passed through a tube heated to bright redness is partly resolved into its elements, carbon being deposited on the sides of the tube, and sulphur passing off with the undecomposed bisulphide. If the tube be filled with lumps of charcoal, the separated sulphur is reconverted into bisulphide (Berthelot, *Zeitschr. f. Chem.* [2] v. 128; Stein, *ibid.* 512).

2. When carbon bisulphide is exposed to sunshine for some months in sealed tubes, a brown substance is deposited, which after a while greatly interferes with the action of the light. If, however, a small quantity of water be introduced into the tubes, this substance is no longer deposited, and the water takes up a small quantity of formic acid:

$$CS^2 + 2H^2O = CH^2O^2 + H^2S + S.$$

On removing the watery layer and the undecomposed bisulphide, a bulky solid substance remains, consisting of carbon sesquisulphide (O. Loew, *ibid.* iv. 622).

3. When a long thin plate of gold or platinum wound into a spiral with *tin-foil* is immersed in carbon bisulphide, the latter is decomposed, sulphur combining with the tin, and carbon being deposited in small crystals (Lionnet, *Compt. rend.* lxiii. 213).

4. The action of carbon bisulphide on various metallic salts at a red heat has been studied by W. Müller (*Pogg. Ann.* cxxvii. 404; *Jahresb.* 1866, p. 120). *Potassium chromate* ignited in a current of the vapour yields potassium trisulphide, chromium sesquisulphide, and gaseous products:

$$2CrO^4K^2 + 5CS^2 = 2K^2S^3 + Cr^2S^3 + 4CO + CO^2 + SO^2.$$

Ammonium chromate yields similar products. *Potassium antimonate* is converted into sulphantimonite, according to the equation:

$$4SbO^3K + 5CS^2 = 4SbS^2K + 3CO^2 + 2CO + 2SO^2.$$

Ammonium antimonate yields an ammonium polysulphide, together with antimonious sulphide. *Potassium manganate* at a strong red heat is converted into potassium trisulphide and manganous sulphide, with evolution of carbon dioxide:

$$MnO^4K^2 + 2CS^2 = K^2S^3 + MnS + 2CO^2.$$

Barium manganate yields similar products. Anhydrous *sodium pyrophosphate* yields sodium metaphosphate and monosulphide, together with carbon monoxide and free sulphur:

$$P^2O^7Na^4 + CS^2 = 2PO^3Na + Na^2S + CO + S.$$

Sodium metaphosphate is not altered under the same circumstances; but *potassium metaphosphate* is decomposed at a higher temperature, with formation of a sulphide of phosphorus.

5. *Oxamide* heated to 180°–200° in sealed tubes with carbon bisulphide, forms ammonium sulphocyanate, carbon oxysulphide, and carbon monoxide:

$$C^2O^2H^4N^2 + CS^2 = CSN.NH^4 + COS + CO.$$

The tubes must be opened from time to time to allow the gases to escape. With *acetamide* the reaction is more complex, a combustible gas not absorbed by cuprous chloride, perhaps methyl, being likewise evolved, according to the equation:

$$2(COCH^3.H^2N) + CS^2 = CSN.NH^4 + COS + CO + (CH^3)^2.$$

If alcohol is added, mercaptan and ethyl bisulphide are also found amongst the products (Ladenburg, *Zeitschr. f. Chem.* [2] v. 478).

6. For the reaction with *sulphuric chlorhydrate* see p. 407.

7. Carbon bisulphide readily dissolves the *chlorides*, *bromides*, and *iodides* of *phosphorus*, *antimony*, *arsenic*, *sulphur*, and *selenium*, also *hydrogen bisulphide*, and mixes with the *tetrachlorides* of *tin* and *titanium*; but the fluorides, chlorides, bromides, iodides, sulphides, and oxides of most metals, and all oxygen salts, are insoluble in it. A solution of *phosphorus* in carbon bisulphide exerts a reducing action; a solution of *bromine* or *iodine*, an oxidising action (Gore, *Phil. Mag.* [2] xxx. 414).

8. Carbon bisulphide may be detected in *coal-gas* by passing the gas (completely

freed from hydrogen sulphide) over red-hot copper-foil. If any bisulphide is present, the copper acquires an iridescent surface, and its nitric acid solution diluted with water yields after some time a precipitate with barium chloride (A. Vogel, *Zeitschr. f. Chem.* [2] vi. 253).

Hydrate of Carbon Bisulphide.—A hydrate $2CS^2.H^2O$ is formed in white crystalline scales when moist carbon bisulphide is strongly cooled by rapid evaporation. It decomposes at about $-3°$, and is therefore as inflammable as the bisulphide itself (Berthelot, *Ann. Ch. Phys.* [3] xlvi. 490; Duclaux, *Bull. Soc. Chim.* [2] viii. 258).

CARBON SESQUISULPHIDE. C^2S^3.—This compound is formed by digesting recently precipitated hydrogen carbosesquisulphide, $H^2C^2S^3$ (*infra*), with strong aqueous ammonia at a gentle heat, and treating the dark red filtered liquid with a current of chlorine. The sesquisulphide is then precipitated, and may be freed from adhering sulphur by means of sodium sulphite, washed with warm water, then with alcohol, and dried. It is also formed when the bisulphide is enclosed, together with water, in sealed tubes and exposed for a long time to the sun's rays (p. 409). It is an amorphous, brown, inodorous powder, insoluble in alcohol, ether, and carbon bisulphide; decomposed into its elements by a heat a little above 200°; not altered by ammonia, soluble without decomposition in boiling potash-ley. It is oxidised by weak nitric acid, yielding an acid, the barium salt of which is soluble in water, the lead and silver salts sparingly soluble. This acid has perhaps the composition $(C^2S^2)''H^2O^2$ corresponding to oxalic acid (O. Loew, *Zeitschr. f. Chem.* [2] i. 722; ii. 173; iv. 623).

Hydrogen Carbosesquisulphide, $C^2S^3H^2$, is produced by agitating carbon bisulphide with pasty sodium-amalgam. On throwing the resulting mass into water, filtering the blood-red solution, passing hydrogen sulphide into it to decompose a mercurial compound, and pouring the liquid into dilute hydrochloric acid, hydrogen sulphide is given off, and a red flocculent substance is precipitated, which when purified by washing with water, dissolution in carbon bisulphide, filtering, and evaporation, has the composition $C^2S^3H^2$. This substance melts at 100° and decomposes at a somewhat higher temperature; it is slightly soluble in alcohol and ether, more freely in carbon bisulphide and in alkaline sulphides.

Hydrogen carbosesquisulphide is an acid, and is analogous in composition to glyoxalic acid, $C^2O^3H^2$; it might therefore be called thioglyoxalic acid. Boiled with *baryta*, it forms the salt BaC^2S^3, which, when treated with hydrochloric acid, reproduces the hydrogen compound. In the same reaction there are formed oxalate, sulphide, and carbomonosulphide of barium, as shown by the equation:

$$2C^2S^3H^2 + 6BaO = C^2O^4Ba + 4BaS + C^2S^2Ba + 2H^2O.$$

The *sodium salt* is formed, together with sodium sulphide, by heating sodium in a sealed tube with carbon bisulphide to 140°-150°. The carbosesquisulphides of the heavy metals are dark-coloured precipitates. The *copper salt*, which has a black-brown colour, is produced when finely divided copper is digested for several hours in sunshine with carbon bisulphide and water (Loew, *loc. cit.*).

Hydrogen carbosesquisulphide is likewise formed by prolonged digestion of phosphorus pentasulphide with acetic acid at 150° in a flask furnished with a condensing tube. The residue left after distillation is washed with water and weak soda-ley, and dissolved in a closed vessel in carbon bisulphide at 120°. The solution when evaporated leaves the compound $C^2S^3H^2$. The portion insoluble in carbon bisulphide is a body which appears to have the composition C^4S; it dissolves with red colour in hot concentrated sulphuric acid and is attacked by nitric acid. Carbon sulphides containing lower proportions of sulphur are likewise formed by the action of phosphorus pentasulphide on many organic bodies (Loew, *Zeitschr.* [2] iii. 20; *Jahresb.* 1867, p. 157).

The action of sodium-amalgam on carbon bisulphide was first examined by Löwig a. Hermann (*Jahresb.* 1860, p. 397), who obtained compounds of sodium with sulphur and carbon of uncertain composition; afterwards by Guignet (*ibid.* p. 122). Girard (*Compt. rend.* xliii. 396) found that nascent hydrogen evolved by zinc and dilute sulphuric acid converted carbon bisulphide into a crystallised compound, CH^2S, volatile at about 150°, and another substance not examined, hydrogen sulphide being at the same time evolved.

CARBONATES. *Ammonia Carbonates.*—An elaborate examination of these salts has lately been made by Divers (*Chem. Soc. J.* [2] viii. 171 [1870]). The main result of this examination is a confirmation of the conclusion arrived at by

Deville (i. 190), that there are three definite ammonium carbonates represented by the following formulæ:

Normal carbonate, $CO^2(NH^3)^2(H^2O)^2 = CO^3(NH^4)^2 + H^2O$

Acid carbonate, $(CO^2)(NH^3)(H^2O) = CO^3\left\{\begin{matrix}NH^4\\H\end{matrix}\right.$

Half-acid or Sesqui-carbonate, $(CO^2)^3(NH^3)^4(OH^2)^4 = (CO^3)^3\left\{\begin{matrix}(NH^4)^4\\H^2\end{matrix}\right. + H^2O$.

The carbonate of ammonia now found in commerce appears to be a mixture or compound of acid carbonate and carbamate, represented by the formula:

$$CO^3(NH^4)H.2[CO^2(NH^2)(NH^4).$$

The preparation, physical properties, and chemical reactions of these salts are fully discussed in the memoir above referred to, which also contains a very complete history of the investigations relating to them.

The acid carbonate occurs below the guano of the Chinca Islands, as a saline deposit smelling of ammonia (Phipson, *Chem. Soc. J.* [2] i. 74).

Barium Carbonate.—The precipitated salt dissolves, under a pressure of 4 to 6 atmospheres, in 132·3 pts. of water saturated with carbonic acid, and is afterwards retained in this solution under ordinary atmospheric pressure. The solution when left to evaporate deposits a heavy precipitate consisting of a mixture of amorphous and crystalline barium carbonate; at the boiling heat the whole of the barium is precipitated as crystalline carbonate. The salt appears, therefore, to be insoluble in water (R. Wagner, *J. pr. Chem.* cii. 233; *Jahresb.* 1867, p. 135).

Calcium Carbonate.—A hydrate containing $CO^3Ca.6H^2O$ is formed on passing carbon dioxide into lime-water or a solution of sugar-lime cooled to between 0° and +2°, or by precipitating calcium chloride with sodium carbonate at the same temperature. The precipitate, flocculent at first, soon becomes crystalline, and after washing with ice-water and drying at 0°, contains 20 p. c. water, answering to the formula above given. At 30° it is quickly converted into a semifluid mixture of water and anhydrous carbonate; at 20° this change takes place somewhat more slowly; and at lower temperatures the salt gradually effloresces. Calcium carbonate precipitated at temperatures above 30° is always anhydrous; between 0° and 30° (*e.g.* at 10°–20°) precipitates are formed, containing quantities of water (10 to 27 p. c.) varying not only with the temperature, but with the time occupied in the precipitation (J. Pelouze, *Bull. Soc. Chim.* [2] iii. 183). *Calcium carbonatochloride*, $CaCl^2.2CaCO^3 + 6H^2O$, was obtained as a sandy crystalline residue on dissolving in water some crystallised calcium chloride which had been prepared on the large scale for technical purposes. The crystals are decomposed by prolonged contact with water, the chloride dissolving and the carbonate remaining in the form of skeletons, which under the microscope appear like aggregates of amorphous spherical masses. The same double salt is formed when a solution of calcium chloride mixed with ammonia is left exposed to the air, its formation being accelerated by excess of carbonic acid in the air above the liquid.

On the solution of calcium carbonate and dolomite in saturated aqueous carbonic acid, see Cossa (*Zeitschr. anal. Chem.* 1869, 145; *Zeitschr. f. Chem.* [2] vi. 89).

Cupric Carbonate.—By dissolving the precipitated basic carbonate in saturated aqueous carbonic acid under a pressure of 4 to 6 atmospheres, a greenish solution is formed containing 1 pt. of the neutral salt CO^3Cu in 4,690 pts., and depositing an amorphous basic salt when heated to boiling. The portion of the original precipitate not dissolved by the aqueous carbonic acid is a greenish crystalline powder having the composition of malachite (Wagner, *loc. cit.*).

Ferrous Carbonate occurs as an amorphous hydrate, $CO^3Fe.H^2O$, in the mines of Pontpéan (Dép. d'Ille-et-Vilaine); white, earthy; but little alterable in the air, and scarcely decomposed by acids at ordinary temperatures (Massieu, *Compt. rend.* lix. 238). Ferrous carbonate (spathic iron) dissolves, under the conditions above specified for the barium salt, in water saturated with carbonic acid, forming a colourless solution which contains 1 pt. in 138 of the normal carbonate, and when heated to boiling deposits a black amorphous precipitate (Wagner).

Indium Carbonate is a white gelatinous precipitate, soluble in ammonium carbonate, reprecipitated on boiling, insoluble in fixed alkaline carbonates. The precipitate formed in indium solutions by alkaline bicarbonates is also soluble in excess of the reagent (Winkler, *J. pr. Chem.* xciv. 1).

Lanthanum carbonate, $2CO^3La.5H^2O$, precipitated from the sulphate by neutral or acid sodium carbonate, and dried at ordinary temperatures, forms micaceous scales having a silky lustre (Hermann, *ibid.* lxxxii. 385).

Lead Carbonates.—The basic salt (white lead) is nearly insoluble in saturated aqueous carbonic acid even under pressure; but the carbonate obtained by precipitation with sodium carbonate is perceptibly soluble therein, 1,000 pts. of the solution containing 0·5 pts. of normal lead carbonate (Wagner). On the formation of carbonato-chloride of lead, see p. 405.

Magnesium Carbonates.—According to Merkel (*Jahresb.* 1867, p. 136), normal magnesium carbonate, CO^3Mg, requires for solution at 5° under pressure of several atmospheres of carbonic acid gas, the following quantities of water:

Atmospheres . . .	1	2	3	4	5	6
Parts of water . .	761	744	134	110·7	110	76

At other temperatures the solubility is in proportion to the quantity of carbon dioxide absorbed by the water.

On the reaction of a mixture of magnesium and calcium chlorides with sodium carbonate, the solubility of the carbonates of calcium and magnesium in solutions of calcium and magnesium salts, and the action of dolomite or gypsum and magnesite in presence of water containing carbonic acid, see T. S. Hunt (*Sill. Am. J.* [2] xlii. 49; *Jahresb.* 1866, 177). On the reaction of basic magnesium carbonate and gypsum with carbonic acid water, see also Gössmann (*Sill. Am. J.* [2] xlii. 217, 368).

Manganous Carbonate.—According to E. Prior (*Zeitschr. anal. Chem.* 1869, 428), the precipitate formed by ammonium carbonate in manganous sulphate has, after drying by pressure, the composition $CO^3Mn.H^2O$, and gives off half its water over oil of vitriol. The precipitate formed by fixed alkaline carbonates in an atmosphere of hydrogen, and dried out of contact with the air, has also the composition CO^3Mn; if precipitated in contact with the air, it contains varying quantities of manganoso-manganic oxide.

Carbonates of Potassium and Sodium.—100 pts. water at 10° dissolve 24·4 pts. of CO^3KH and 8·3 pts of CO^3NaH (G. J. Mulder, *Jahresb.* 1866, p. 87).

The double salt $CO^3KNa.6H^2O$, which Marignac obtained by crystallising a solution containing equivalent quantities of the component salts, has been obtained by Stolba (*Bull. Soc. Chim.* [2] iv. 192) in purifying the potash of beet-molasses. The salt is decomposed by recrystallisation, yielding crystals containing larger proportions of sodium carbonate and water, and a mother-liquor richer in potassium carbonate. From a solution containing excess of potassium carbonate, however, the double salt may be crystallised without alteration (see further *Bull. Soc. Chim.* [2] vii. 241; *Jahresb.* 1866, p. 156).

Crystallised *sodio-calcic carbonate*, $(CO^3)^2CaNa^2.5H^2O$ (*Gay-Lussite*), is formed on mixing an excess of a saturated solution of sodium carbonate (sp. gr. 1·185 to 1·200), with a solution of calcium chloride (sp. gr. 1·13 to 1·15); the best proportions are 10 vol. of the former to 1 vol. of the latter. The liquid gelatinous mass at first produced, quickly changes to a sediment composed of well-defined crystals, which are monoclinic like those of the native mineral; when quickly formed, they exhibit the combination ∞P . $-P$; when more slowly deposited (from somewhat weaker solutions), they are usually larger, and exhibit only the two hemipyramids $+P$ and $-P$ (Fritzsche, *J. pr. Chem.* xciii. 339; *Jahresb.* 1864, p. 190).

Rubidium Carbonate, CO^3Rb^2 (v. 131).

Silver Carbonate, CO^3Ag^2, separates in crystals from a solution of 1 grm. silver nitrate in 15 grms. water mixed with 1·156 grm. sodium hydrate in 20 pts. water, and then with ammonia added by drops; the liquid first deposits crystallised silver oxide, and afterwards crystals of the carbonate (H. Vogel, *J. pr. Chem.* lxxxvii. 288; *Jahresb.* 1862, p. 228).

Thallium Carbonate, CO^3Tl^2.—See THALLIUM-SALTS (v. 753).

Thorinum Carbonate, $(CO^3)^2Th$ (v. 787).

Zinc Carbonate.—By dissolving the precipitated basic salt in saturated aqueous carbonic acid prepared under a pressure of 4 to 6 atmospheres, a solution is formed containing 1 pt. of the neutral carbonate CO^3Zn in 189 pts.; it becomes turbid under ordinary pressure, and deposits amorphous basic salt both by spontaneous evaporation and at the boiling heat (Wagner).

Carbonic Ethers. *Ethyl carbonate*, $CO^3(C^2H^5)^2$, is formed, together with carbon monoxide and alcohol, by the action of sodium ethylate or potassium ethylate on ethyl oxalate. In its formation from the latter by the action of sodium or potassium, it is probable that ethylate of sodium or potassium is first formed, and then reacts as above (Cranston a. Dittmar, *Chem. Soc. J.* [2] vii. 441). See OXALIC ETHERS in this volume.

Ethyl carbonate, saturated with *hydrobromic acid* and heated to 100°, is resolved into ethyl bromide, carbon dioxide, and water (H. Gal, *Compt. rend.* lix. 1049). With *sodium* it yields sodium-ethylcarbonate, ethyl oxide, and carbon monoxide:

$$3CO^3(C^2H^5)^2 + Na^2 = 2CO^3C^2H^5Na + 2(C^2H^5)^2O + CO.$$

The same products are obtained when ethyl carbonate is heated with sodium ethylate in a sealed tube (Geuther, *Zeitschr. f. Chem.* [2] iv. 658).

Ethyl-phenyl carbonate, $CO^3\left\{\begin{matrix}C^2H^5\\C^6H^5\end{matrix}\right.$, produced by the action of potassium phenate on ethyl chlorocarbonate (p. 406), and separated from the warmed mixture by water, is a transparent, colourless, strongly refracting liquid, having an aromatic odour, resembling also that of phenol, a sp. gr. of 1·117 at 0°, and boiling (though not constantly) at 234°. By boiling with baryta-water, it is resolved into ethyl alcohol, phenol, and carbon dioxide, without formation of salicylic acid (Fatianoff, *Zeitschr. Ch. Pharm.* 1864, p. 77).

Ethyl orthocarbonate, $CO^4(C^2H^5)^4$ or $C(OC^2H^5)^4$, discovered by Bassett, is described in vol. iv. p. 238.

CARBONAPHTHALIC ACID. Syn. with NAPHTHYL-CARBONIC ACID (*q.v.*).

CARBONUSNIC ACID. $C^{19}H^{16}O^8$.—An acid nearly related to usnic acid, ($C^{18}H^{18}O^7$), existing in *Usnea barbata*, Hoffm., a lichen which grows on cinchona bark. It is extracted by treating the lichen with milk of lime and with alcohol, precipitating the resulting solution of the calcium salt with hydrochloric acid, and recrystallising from ether. It forms sulphur-yellow prisms, insoluble in water, slightly soluble in alcohol, dissolving in 334 pts. ether at 20°. From solution in alkalis or lime-water, it is precipitated by carbonic acid; not coloured by chloride of lime. Melts at 195·4° (usnic acid at 201·8°). When boiled with alcohol or treated with baryta-water in sunshine, it is resolved into carbon dioxide and an acid precipitated by hydrochloric acid and crystallising in prisms; perhaps evernic acid (O. Hesse, *Ann. Ch. Pharm.* cxxxvii. 241).

CARBONYL-DISULPHODIETHYL. $CO(SC^2H^5)^2$.—A compound isomeric with xanthic ether, produced by the action of strong sulphuric acid on ethyl sulphocyanate (Schmitt a. Glutz, *Zeitschr. f. Chem.* [2] iv. 723). See SULPHOCARBONIC ETHERS.

CARBOPYROLAMIDE. Syn. with DIPYROMUCAMIDE. See PYROMUCIC ACID, AMIDES OF (iv. 765).

CARBOXYL, COOH; also called *Oxatyl.*—A radicle supposed to enter into the composition of organic acids (p. 38).

CARBOXYLIC ACID. $C^{10}H^4O^{10}$.—An acid formed by oxidation of the hydrocarboxylic acids (iii. 189; iv. 296).

CARBYLAMINES. See CYANIDES, ALCOHOLIC.

CARMENITE. A copper ore approaching nearly in composition to $Cu^2S.CuS$, occurring, together with red copper ore, malachite, and tile ore, on the island of Carmen, in the Gulf of California. It is massive, imperfectly cleavable, of dark steel-blue colour; hardness 3·5, and sp. gr. 5·29 (Hahn, *Jahresb.* 1865, p. 868).

CARMINE-RED, See the next article.

CARMINIC ACID (i. 804). C. Schaller (*Bull. Soc. Chim.* [2] ii. 414) prepares this acid by precipitating the aqueous extract of cochineal with neutral lead acetate slightly acidulated with acetic acid; decomposing the washed precipitate with sulphuric acid; again precipitating the filtrate with lead acetate, and decomposing the precipitate with sulphuric acid, avoiding an excess; then precipitating a third time, and decomposing this precipitate with hydrogen sulphide. The filtered solution is evaporated to dryness; the residue dissolved in absolute alcohol; the crystalline nodules of carminic acid obtained on leaving this solution to evaporate are freed from a yellow substance by washing with cold water, which dissolves only the carminic acid; and the residue left on evaporating the aqueous solution is recrystallised from absolute alcohol or from ether. Schaller assigns to carminic acid the formula $C^9H^{12}O^6$, differing by H^2O from that given by Schützenberger, $C^9H^{10}O^5$ (i. 804). It is bibasic, forming acid and neutral salts. The neutral sodium salt is obtained by mixing the solutions of the acid and of caustic soda in absolute alcohol, as a precipitate which crystallises from water in nodular groups.

According to Hlasiwetz and Grabowski (*Ann. Ch. Pharm.* cxli. 129), on the other hand, the composition of carminic acid is represented by the formula $C^{17}H^{18}O^{10}$. With potash in alcoholic solution it forms a red, afterwards dark violet precipitate, which when washed with alcohol out of contact with the air dries up to a dark violet mass, having when dried at 120°–130° the composition $2C^{17}H^{16}O^{10}K^{2}.H^{2}O$. The purple-red aqueous solution of this salt is precipitated by the chlorides of barium, strontium, and calcium; the barium-compound dried at 130° consists of $C^{17}H^{16}O^{10}Ba$.

Carminic acid is a glucoside, and is resolved by boiling with dilute acids into carmine-red and sugar:

$$\underset{\text{Carminic acid.}}{C^{17}H^{18}O^{10}} + 2H^{2}O = \underset{\text{Carmine-red.}}{C^{11}H^{12}O^{7}} + \underset{\text{Sugar.}}{C^{6}H^{10}O^{5}}$$

To obtain these products of decomposition, the dark violet precipitate formed by lead acetate in a filtered decoction of cochineal, after being carefully washed, is decomposed with dilute sulphuric acid, and the dark red filtrate, completely freed from lead by hydrogen sulphide, is boiled for several hours in a flask having an upright condenser with sulphuric acid (10 c.c. of the concentrated acid to 1 pound of cochineal). The liquid is then mixed with levigated barium carbonate till both the precipitate and the liquid assume a violet colour; the liquid is filtered as quickly as possible; and the filtrate is precipitated with neutral lead acetate. The precipitate (A) contains the carmine-red; the liquid (B), which is mostly reddish, contains the sugar. The solution freed from lead by hydrogen sulphide and cautiously evaporated—best under the air-pump—leaves a honey-yellow syrup, from which alcohol throws down a sugar-barium compound, $(C^{6}H^{9}O^{5})^{2}Ba$, in white flocks which become gummy in drying. The sugar separated therefrom has the composition $C^{6}H^{10}O^{5}$ at 50°, and $C^{6}H^{8}O^{4}$ at 100°. It is a honey-yellow, amorphous, hygroscopic mass, having a faint odour of caramel and a bitterish taste; easily reduces cupric oxide in alkaline solution; exhibits Pettenkofer's reaction with bile, even in very small quantity; is nearly insoluble in alcohol, unfermentable and optically inactive.

To separate the carmine-red, the precipitate (A) stirred up with water is treated with dilute hydrochloric acid, till, on adding the acid by drops, the colour of the liquid, which has become scarlet, suffers no further alteration. The filtrate freed from lead by hydrogen sulphide is then evaporated at a gentle heat; the residue is dissolved in cold water; and the solution is perfectly dried over sulphuric acid under the air-pump. Pure carmine-red, $C^{11}H^{12}O^{7}$, is thus obtained as a dark purple-red shining mass with green reflex, triturable to a very slightly hygroscopic powder, soluble with fine red colour in water and in alcohol, insoluble in ether. When burnt, it leaves a trace of ash, consisting of lime, iron, and phosphoric acid. On mixing the alcoholic solution of carmine-red with an alcoholic solution of potash, a potassium salt $C^{11}H^{10}O^{7}K^{2}$ is precipitated, with red colour changing to dark violet. The aqueous solution of this salt gives, with barium chloride, calcium chloride, and zinc sulphate, dark violet precipitates containing respectively $C^{11}H^{10}O^{7}Ba$, $C^{11}H^{10}O^{7}Ca$, and $C^{11}H^{10}O^{7}Zn$. Another zinc compound, $(C^{11}H^{11}O^{7})^{2}Zn$, is deposited on leaving a solution of carmine-red (or carminic acid) in contact with dilute sulphuric acid and excess of zinc, as a pulverulent mass exhibiting a green translucence. A solution of carmine-red boiled with zinc and sulphuric acid, or warmed with sodium-amalgam out of contact with air, becomes almost colourless, yielding easily decomposible products.

Coccinin, $C^{14}H^{12}O^{5}$, is formed, together with oxalic, succinic, and probably acetic acid, by fusing carmine-red with 3 pts. of potassium hydrate liquefied with a little water (or crude carminic acid with 4 or 5 pts. potash) till a sample of the fused mass dissolves in water with gold-brown colour. By decomposing the aqueous solution of the product with dilute sulphuric acid, filtering to separate a resinous substance, agitating the filtrate with ether, and evaporating the ethereal solution, a crystalline residue is obtained from which water extracts the above-mentioned acids, leaving the coccinin (which is formed only in small quantity) undissolved. The coccinin, when freed by pressure from a brown extractive matter and recrystallised from hot dilute alcohol, forms yellow micaceous laminæ having a greenish tinge in the mass, but appearing under the microscope as straw-yellow rectangular tablets, apparently belonging to the rhombic system, and exhibiting the colour-phenomena of polarising crystals.

It is insoluble in water, easily soluble in alcohol, sparingly in ether, very soluble in dilute alkalis. The alkaline solution is yellow at first, but on exposure to the air becomes green, then violet, and at last purple-red; the solution in ammoniacal water soon turns violet when agitated with air; the alcoholic solution is coloured red by ferric chloride. The solution in strong sulphuric acid, which is yellow in the cold, becomes indigo-blue when warmed or on addition of a few grains of manganese dioxide.

With sodium-amalgam, the alcoholic solution immediately deposits flocks, turns green and then dark blue on exposure to the air, a dark blue amorphous body being at the same time deposited. An ammoniacal compound of coccinin, $C^{14}H^{12}O^5 . NH^3$, is formed on passing ammonia gas over the dried substance; the alcoholic solution gives with lead acetate a yellowish precipitate quickly changing to violet (Hlasiwetz a. Grabowski).

CARNAÜBA WAX. See Canaüba Wax (p. 391).

CARNALLITE, $KCl . MgCl^2 . 6H^2O$, is found in the rock-salt formation of Maman in Persia (Göbel, *J. pr. Chem.* xcvii. 6; *Jahresb.* 1865, p. 912).

CARTHAMIN. According to Malin (*Ann. Ch. Pharm.* cxxxvi. 115), this colouring matter, fused with potash till hydrogen is rapidly given off and the aqueous solution of the mass is no longer precipitated by acids, yields paraoxybenzoic acid, together with oxalic acid:

$$\underset{\text{Carthamin.}}{C^{14}H^{16}O^7} + O = 2\underset{\text{Para-oxy-benzoic acid.}}{C^7H^6O^3} + 2H^2O.$$

CARVIOLIN. A substance which separates from the concentrated aqueous extract of cauliflower and other species of Brassica, in microscopic leaf-like crystals, which on addition of alcohol to the solution, change into granules grouped in hexagonal masses (H. Reinsch, *N. Jahrb. Pharm.* xxvi. 196; xxvii. 197; *Jahresb.* 1866, p. 705; 1867, 767).

CARVOL. $C^{10}H^{14}O$.—Carvol from oil of caraway does not unite with potash, but is converted by it into the isomeric compound carvacrol. When vapour of carvol is passed over heated zinc-dust (metallic zinc, oxide and hydrate), two hydrocarbons are obtained, viz. $C^{10}H^{16}$, boiling, after distillation over sodium, at 173°, and $C^{10}H^{20}$, boiling at 176°–178°. The hydrocarbon $C^{10}H^{16}$ is oxidised by chromic acid to terephthalic acid, whereas carvene from oil of caraway (i. 809) yields by the same treatment oxalic acid and a resin. This hydrocarbon gives also with fuming sulphuric acid a sulpho-acid identical with that obtained from cymene (Arndt, *Zeitschr. f. Chem.* [2] iv. 730).

CASCARILLINE. A base obtained from cascarilla bark (from *Croton eleuteria*), and allied in its properties to ricinine (Tuson, *Chem. Soc. J.* [2] ii. 195).

CASEIN. See Proteides.

CASSUVIUM POMIFERUM. The kernels of this tree, called *Acajou nuts*, yield 41·8 p. c. of a sweet pale yellow oil, of sp. gr. 0·916. The pericarp yields 35 p. c. of a white viscid vesicating oil, of sp. gr. 1·014; this oil becomes dark-coloured on exposure to the air; reddens litmus; dyes linen permanently yellow-red; and dissolves in alcohol and ether, leaving a white flocculent substance (J. Lepine, *J. Pharm.* [3] xl. 16).

CASTANEA. See Chestnut.

CASTELLITE. A mineral from Guanasevi in Mexico, massive, variegated on the surface, distinctly laminar, and having a sp. gr. of 5·186 to 5·241. Gives by analysis:

S	Cu	Ag	Pb	Zn	Fe	
25·65	41·14	4·64	10·04	12·09	6·49	= 100·05,

a composition which may be represented by the formula $(Cu';Ag)^2S . 2(Cu;Pb;Zn;Fe)S$ (Rammelsberg, *Jahresb.* 1866, p. 917).

CATASPILITE. A mineral from the Langbans iron mines, in Wermland, Sweden, where it occurs imbedded in grey chlorite. It has the crystalline form of cordierite, and appears to be a product of the alteration of that mineral. Ash-grey, translucent at the thin edges, gradually turning red on exposure to the air. Hardness = 2·5;

SiO^2	Al^2O^3 *	CaO	MgO	K^2O	Na^2O	Loss by ignition
40·05	28·95	7·43	8·20	6·90	5·25	3·22 to 1·0:

whence the formula $9[2(M'';M^2)O . SiO^2] + 5(2\overset{vi}{M}{}^2O^3 . 3SiO^2)$ (Igelström, *Jahresb.* 1867, p. 983).

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* With a small quantity of ferric oxide.

CATECHIN (Zwenger, *Ann. Ch. Pharm.* xxxvii. 320; Neubauer, *ibid.* xcvi. 337; Kraut a. van Delden, *ibid.* cxxviii. 285; Hlasiwetz a. Malin, *ibid.* cxxxiv. 118; Schützenberger a. Rack, *Bull. Soc. Chim.* [2] iv. 5).—This substance gives by analysis, in the air-dried state, about 52 p. c. carbon and 6 p. c. hydrogen; dried at 100°, about 61·4 p. c. carbon and 5·0 hydrogen. These numbers agree approximately with the following formulæ, by which catechin dried at 100° has been represented by different chemists:

Zwenger	Neubauer	Hlasiwetz a. Malin	Schützenberger a. Rack		
$C^{20}H^{18}O^{8}$	$C^{17}H^{18}O^{7}$	$C^{19}H^{18}O^{8}$	$C^{10}H^{10}O^{4}$	$C^{12}H^{12}O^{5}$	$C^{22}H^{22}O^{9}$.

Kraut a. van Delden also represents catechin dried at 100° by the formula $C^{12}H^{12}O^{5}$, and the air-dried substance by $C^{12}H^{12}O^{5}.2H^{2}O$.

Catechin melted with *potassium hydrate* is resolved into protocatechuic acid and phloroglucin (Hlasiwetz a. Malin):

$$\underset{\text{Catechin.}}{C^{19}H^{18}O^{8}} + O^{2} = \underset{\text{Protocatechuic acid.}}{C^{7}H^{6}O^{4}} + \underset{\text{Phloroglucin.}}{2C^{6}H^{6}O^{3}}$$

Kino, which contains catechin, yields by similar treatment 12 p. c. phloroglucin, and is, according to Hlasiwetz, the best material for the preparation of that compound.

Catechin boiled with dilute *sulphuric acid* out of contact with the air, or with alcohol containing *hydrochloric acid*, is converted into a brown amorphous powder called catechuretin, insoluble in water and in alcohol. This substance appears to be formed from catechin by dehydration and [according to the formula of catechin given by Hlasiwetz] its formation may be represented by the equation:

$$\underset{\text{Catechin.}}{C^{19}H^{18}O^{8}} - 2H^{2}O = \underset{\text{Catechuretin.}}{C^{19}H^{14}O^{6}}$$

Catechuretin treated with bromine-water is converted into reddish insoluble bromocatechuretin (Kraut a. van Delden). These chemists give for catechuretin the formula $C^{12}H^{10}O^{4}$ (= $C^{12}H^{12}O^{5} - H^{2}O$), and for bromocatechuretin, $C^{12}H^{6}Br^{4}O^{4}$. According to Sacc (*Compt. rend.* liii. 1102), an aqueous solution of catechu heated to 100° for an hour with sulphuric acid deposits a brown powder insoluble in water, alcohol, ether, and acids (doubtless catechuretin), and the filtered liquid neutralised with calcium carbonate yields, on addition of alcohol, a precipitate consisting of the tartrates of calcium and sodium, and a filtrate which on evaporation leaves a residue of glucose.

Catechin heated to 190° with *benzoyl chloride* yields two brown products, one soluble in alcohol, and having the composition of monobenzoyl-catechin, the other insoluble, derived in like manner from catechuretin. Catechin heated to 100° with water and *phosphorous iodide*, PI^{3}, forms a solution which gradually deposits a yellow elastic substance insoluble in water, alcohol, ether, and glacial acetic acid, and agreeing approximately with the formula $C^{22}H^{22}O^{8}$ [or $C^{19}H^{18}O^{7}$]. When a solution of catechin in *acetic anhydride* is mixed with pulverised *barium peroxide*, and then with water, a white substance is precipitated, which when freed from baryta by repeated solution in glacial acetic acid and precipitation with water, has the composition $C^{21}H^{14}O^{10}$ [or $C^{19}H^{12}O^{9}$]. A brown substance of the same or nearly the same composition (called *japonic acid*) is obtained by oxidising catechin with potassium bichromate (Schützenberger a. Rack).

CATECHU, ACIDS OF (J. Loewe, *J. pr. Chem.* cv. 32, 75; *Zeitschr. f. Chem.* [2] v. 538).—1. CATECHUIC ACID, $C^{16}H^{14}O^{6}$. To prepare this acid, pulverised catechu is boiled with water; the solution is left to stand for some days; the crystals which separate are dissolved in water containing acetic acid; the solution is precipitated with lead acetate; and the filtered liquid, after being freed from lead by hydrogen sulphide, is left to crystallise in a dark place. Catechuic acid is thus obtained in concentric groups of white microscopic needles, having the composition $2C^{16}H^{14}O^{6}.H^{2}O$, which give off their water of crystallisation at 100°–160°, and decompose at a higher temperature.

The solution of catechuic acid in alkalis is colourless at first, but soon turns yellow. On addition of acetic acid the colour becomes lighter, and the solution then gives a precipitate with gelatin. Ferric chloride colours the solution of catechuic acid chrome-green, and afterwards forms a brown precipitate. With sodium acetate and ferric chloride an indigo-blue colour is produced. Mercuric chloride produces a white turbidity, soluble in hydrochloric acid; cupric acetate throws down brown flocks. No precipitate is formed by zinc acetate, potassium ferro- or ferri-cyanide, gelatin, alkaloïds, or tartar-emetic. Silver nitrate is decomposed, with separation of metallic silver. ' Potassium dichromate forms a red-brown precipitate. Solutions of catechuic acid turn brown on exposure to the air, and are then precipitated by gelatin. When boiled with acids, it deposits a brown powder consisting of catechuretin, which, according to Loewe, has the composition $C^{14}H^{12}O^{10}$. The liquid filtered from this precipitate contains catechutannic acid, but no sugar.

2. Catechutannic Acid. $C^{18}H^{14}O^{8}$.—The aqueous extract of catechu is evaporated; the residue exhausted with alcohol; and the filtered alcoholic solution is freed from lime with sulphuric acid, then treated with lead carbonate, finally purified with hydrogen sulphide, evaporated to a syrup, mixed with water, and evaporated to dryness. The residue is then dissolved in alcohol; the solution mixed with ether, which produces a precipitate; the filtered ethereal solution evaporated; the residue moistened with water; and the resulting aqueous solution filtered from catechuic acid, which crystallises out, and from catechin by repeated agitation with ether, which dissolves the latter. On finally evaporating the solution thus purified, catechutannic acid is obtained as a gummy, easily friable mass, very soluble in water, insoluble in ether, sparingly soluble in a mixture of ether and alcohol. Its aqueous solution gives an immediate precipitate with gelatin, tartar-emetic, alkaloïds, ferric chloride either alone or mixed with sodium acetate, also with cupric acetate and zinc acetate; it reduces silver nitrate, and forms with potassium dichromate a brown-red precipitate, with mercurous nitrate a white, with platinic chloride a yellow, and with auric chloride a brown precipitate, after a while also metallic gold. Hydrochloric acid added to the solution throws down yellow flocks; sulphuric acid resinises pulverulent catechutannic acid, but after the latter has absorbed water, forms a yellow powder. The solution of catechutannic acid is coloured brown by caustic alkalis, becomes lighter on addition of acetic acid, and then yields with lead acetate a precipitate which quickly turns brown. The acid dissolves in ammonia, and the solution dries up over sulphuric acid to a varnish, which dissolves in water, is precipitated by acetic acid, but is not altered by gelatin. Catechutannic acid when heated gives off water, and then a yellow liquid which solidifies to small prisms (pyrocatechin ?). On boiling the acid with water containing 2 p. c. sulphuric acid, a brown resinous body separates, which when washed with water and dissolved in alcohol leaves on evaporation a gummy mass having the composition $C^{18}H^{12}O^{5}$. Catechutannic acid is absorbed by animal membranes.

3. The precipitate formed by ether in the alcoholic solution of catechutannic acid contains two compounds, $C^{14}H^{12}O^{6}$ and $C^{14}H^{14}O^{6}$, agreeing in their properties with the japonic and rubinic acids described by Svanberg (iii. 442; v. 182).

The portion of the aqueous extract of catechu which is insoluble in alcohol dissolves partially in alcohol containing sulphuric acid; and on removing the sulphuric acid from the solution by lead carbonate, the lead by hydrogen sulphide, and evaporating the filtrate to dryness, a residue is obtained only a part of which dissolves on boiling with water, the remainder being however soluble in alcohol. The residue left on evaporating the alcoholic solution thus obtained has the composition $2C^{16}H^{28}O^{5}.H^{2}O$, and is designated by Loewe as mimotannihydroretin. The aqueous solution when boiled also deposits brown flocks, which are likewise soluble in alcohol, and the resulting alcoholic solution leaves on evaporation a substance called mimotanniretin, having the composition $C^{14}H^{12}O^{6}$.

Finally, Loewe confirms the observation of Runge, that on agitating an aqueous solution of catechuic acid with ether, and evaporating the ether, a base is obtained in combination with tannic acid.

CATECHURETIN. See Catechin, p. 416.

CATHARTIC ACID. $C^{180}H^{192}N^{4}O^{82}S$?—This, according to Dragendorff a. Kubly (*Bull. Soc. Chim.* [2] vii. 356), is the active principle of senna-leaves, in which it exists partly in combination with lime and magnesia. To prepare it, the aqueous extract of the leaves, evaporated to a syrup, is mixed with an equal volume of alcohol, and the liquid, filtered from the mucus and salts thereby separated, is mixed with absolute alcohol as long as a precipitate is formed. The aqueous solution of this precipitate, purified by a second precipitation with alcohol, and freed from albuminous substances by a few drops of hydrochloric acid, yields, on further addition of hydrochloric acid, a precipitate of cathartic acid, which may be purified by precipitation with ether from the alcoholic solution.

Cathartic acid thus obtained is an amorphous substance, brown while moist, black after drying, soluble in alkalis, and precipitable therefrom by acids. It is a glucoside, and is resolved, by boiling with acids in alcoholic solution, into sugar and a yellow-brown powder, insoluble in water and in ether, called cathartogenic acid. Dragendorff a. Kubly represent the decomposition by the following equation:

$$\underset{\text{Cathartic acid.}}{C^{180}H^{192}N^4O^{82}S} + 10H^2O = \underset{\text{Cathartogenic acid.}}{C^{132}H^{116}N^4O^{44}S} + \underset{\text{Sugar.}}{8C^6H^{12}O^6}$$

It must be observed, however, that neither cathartic nor cathartogenic acid has yet been obtained sufficiently pure to enable their composition to be determined by analysis: hence the preceding equation is to a great extent conjectural.

The alcoholic liquids obtained in the preparation of cathartic acid contain a reddish-brown substance soluble in ether, and resembling chrysophanic acid; and in the portion insoluble in ether (together with Ludwig's sennepicrin, *q.v.*) a crystallisable saccharine substance, $C^{21}H^{44}O^{19}$(?), called cathartomannite. This substance is unfermentable, optically dextrogyrate, and does not reduce an alkaline cupric solution, even after several days' contact with dilute sulphuric acid.

CATHARTOGENIC ACID. }
CATHARTOMANNITE. } See the preceding article.

CAVIARE. See EGG.

CEDRELA. The bark of *Cedrela febrifuga*, used in Java as a febrifuge, contains—besides starch, wax, oxalic acid, citric acid, and a non-crystallisable bitter principle—a body, $C^{16}H^{16}O^4$, resembling phlobaphene, and an iron-greening tannin, called cedrela-tannic acid, which appears, from the analysis of its lead-salt, to have the composition $C^{17}H^{20}O^{11}$, analogous to that of cinchona-tannic acid (W. Lindau, *Jahresb.* 1861, p. 768).

CELLULOSE. $nC^6H^{10}O^5$.—This compound, or a modification of it, exists, according to De Luca (*Compt. rend.* lii. 102; lvii. 43), in the skin of the silkworm and of serpents, and according to Béchamp (*ibid.* lxv. 42) in the vibrating corpuscles of the silkworm. These animal substances, boiled with strong potash-ley, yield a non-azotised body insoluble therein, but dissolving in cold strong sulphuric acid, and forming a jelly which by prolonged boiling with water is converted into fermentable sugar.

Cellulose is formed from drupose (a substance obtained by the action of boiling hydrochloric acid on glycodrupose, which constitutes the stony concretions occurring in pears) by boiling with dilute nitric acid:

$$\underset{\text{Drupose.}}{C^{12}H^{20}O^8} + O^2 + H^2O = \underset{\text{Cellulose.}}{C^6H^{10}O^5} + \underset{\text{Glucose.}}{C^6H^{12}O^6}$$

Also, though in smaller quantity, by similar treatment of glycodrupose itself (J. Erdmann, *Ann. Ch. Pharm.* cxxxviii. 1). See GLYCODRUPOSE.

Pure cellulose is easily prepared from the pith of various plants (e.g. *Phytolacca dioïca* and *Aralia papyrifera*) by macerating it for eight to fourteen days in a mixture of 1 vol. hydrochloric acid and 9 vol. water, washing the undissolved matter with water, and then with aqueous ammonia (Payen, *Ann. Ch. Phys.* [4] vii. 382; *Zeitschr. f. Chem.* [2] ii. 334). See further Payen (*Compt. rend.* lxiv. 1167; *Jahresb.* 1867, p. 952).

According to E. Mulder (*Scheik. Onderz.* III. deel, tweede stuk, Onderz. 145; *Jahresb.* 1863, p. 565), the solution of cellulose in cuprammonia (i. 820) gives with lead acetate a precipitate containing cellulose and lead oxide in varying proportions; by digestion with finely divided lead oxide, the same solution yields the compound $C^6H^1\ O^5.PbO$. With potash, soda, baryta, and lime, blue gelatinous precipitates are obtained. Mulder represents the compound of cellulose and cuprammonia by the formula $(C^6H^{10}O^5)^2Cu(NH^4)^2O$, and supposes the blue precipitates just mentioned to have the composition $(C^6H^{10}O^5)^2CuK^2O$, $(C^6H^{10}O^5)^2CuBaO$, &c. Zinc added to a solution of cellulose in cuprammonia precipitates the copper and forms a colourless liquid similar in its chemical properties to the original solution, and quite inactive to polarised light.

Mulder has also observed that when pure (Swedish) filter-paper is heated with water to 200°, a small quantity of glucose is produced.

Acetyl-cellulose.—Cellulose (cotton or Swedish filter-paper) heated to 180° in sealed tubes with six to eight times its weight of acetic anhydride, dissolves to a thick syrup, which when poured into water deposits white flocks of triacetocellulose, $C^6H^7(C^2H^3O)^3O^5$. This compound is insoluble in water, alcohol, and ether, soluble in strong acetic acid, and easily saponified by alkalis, with reproduction of cellulose. No more highly acetylated compound is formed, however long the heat may be continued, or however great an excess of acetic anhydride may be employed. Hence cellulose,

$C^6H^{10}O^5$, appears to be a triatomic alcohol.* Cotton heated to only 150° with 2 mol. acetic anhydride swells up without dissolving, and yields a mixture of mono- and di-acetyl-cellulose, which have not yet been separated (Schützenberger a. Naudin, *Compt. rend.* lxviii. 814; *Zeitschr. f. Chem.* [2] v. 264).

FULMINOSE.—This name is applied by Blondeau (*Ann. Ch. Phys.* [3] xviii. 462; *Jahresb.* 1863, p. 567) to an isomeric modification of cellulose, which, according to his observations, is produced by boiling gun-cotton with ammonium sulphide; also by the action of concentrated acids, or even of heat alone, on cellulose, and forms the chief constituent of parchment-paper (i. 819). It is not altered by contact with water, acids, or alkalis; in fuming nitric acid it does not dissolve like ordinary paper, but is converted into a nitro-compound. When heated for some time to 100°, it becomes so brittle that it may be pulverised; at 140° it is immediately resolved into water and a porous, very easily combustible charcoal. A piece of calico placed between hot bricks is converted, without alteration of external appearance, into a very friable substance, which burns like tinder. Fulminose decomposes at the same temperature as gun-cotton; it dissolves in a mixture of alcohol and ether, also in acetic acid, and is converted by acetic acid into a gelatinous mass.

CERBERIN. A glucoside existing in solution in the poisonous oil of *Cerbera Odollam*, an East Indian plant, and separating in the crystalline form from the alcoholic solution of the oil (Oudemans, *J. pr. Chem.* xcix. 407).

CERIUM. *Atomic weight* 92.—Wöhler (*Ann. Ch. Pharm.* cxliv. 251) prepares metallic cerium as follows: The hydrochloric acid solution of crude brown cerium oxide (obtained by igniting the mixed oxalates of cerium, lanthanum, and didymium) was mixed with about an equal weight of potassium chloride and sal-ammoniac, evaporated to dryness, heated as long as sal-ammoniac continued to be given off, and fused. The fused mass (which was perfectly soluble in water) was pulverised, mixed while still warm with small pieces of sodium, thrown into a red-hot earthenware crucible, and after the reaction had commenced, heated till the sodium flame disappeared, but no longer. The cooled mass contained numerous small metallic globules, which were picked out, or separated by lixiviation with cold water. Larger and more numerous globules were obtained by placing the sodium in a single lump on the bottom of the ignited crucible, covered with potassium carbonate, and shaking the pulverised saline mass upon it. The metal thus prepared, which appears to consist mainly of cerium [doubtless containing small quantities of lanthanum and didymium, and perhaps also potassium and sodium] is intermediate in colour between iron and lead, and has a bright lustre on polished surfaces, but acquires a blue tarnish on exposure to the air. It is malleable, may be flattened and melted almost like lead, and has a sp. gr. of 5·5 at 12°. Heated to redness before the blowpipe, the fused metal burns with a glimmering light to a brown oxide, and at a stronger heat burns explosively with very brilliant sparks; the pulverised unfused metal takes fire even below 100°. With water it produces a slight disengagement of hydrogen at the boiling heat; hydrochloric acid dissolves it with violent action; strong nitric acid converts it into brown cerium oxide; dilute nitric acid dissolves it readily.

The saline mass which served as matrix to the metallic cerium was accompanied by shining scales of an oxychloride, $CeCl^2 . 2CeO$ or $Ce^3Cl^2O^2$.

Preparation of pure Cerium salts.—Bunsen's method (i. 832) has been modified as follows by Czudnowicz (*J. pr. Chem.* lxxx. 16): The mixture of ceroso-ceric, magnesic, lanthanic, and didymic nitrates is cautiously heated to 230°–300°, with continual agitation, the salts then fusing in their water of crystallisation, and afterwards giving off nitrous vapours. As soon as brown oxide of cerium begins to separate at the bottom of the capsule, the mass is left to cool, and treated first with a large quantity of boiling water, then with water containing nitric oxide, whereby basic ceroso-ceric nitrate is separated, which is to be purified by decantation. The decanted liquids are evaporated to crystallisation, and the crystals are treated as above. In this manner the whole of the cerium present is obtained in the form of basic ceroso-ceric nitrate, which when ignited yields pure ceroso-ceric oxide. See also Holtzmann (*Zeitschr. Ch. Pharm.* 1862, p. 668; *Jahresb.* 1862, p. 136). Popp (*Ann. Ch. Pharm.* cxxxi. 361) mixes the solution of crude cerium oxide with sodium acetate, and passes chlorine gas into it, or treats it with sodium hypochlorite, whereby a precipitate of a hydrated peroxide (CeO^2, according to Popp) is obtained free from lanthanum and didymium. This is but a slight modification of the original mode of separation given by

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* The composition of the nitrylated derivatives of cellulose (PYROXYLINS, iv. 777) would seem to show that the true formula of cellulose is $C^{18}H^{30}O^{15}$; if so, the compound above described must be $C^{18}H^{22}(C^2H^3O)^8O^{15}$.

Mosander (i. 831). Pattison a. Clark (*Chem. News*, xvi. 259) dissolve the crude oxide of cerium in aqueous chromic acid, evaporate to dryness, and heat the residue to 110°. On subsequently treating it with water, the didymium and lanthanum dissolve, while a pure cerium oxide remains in the form of a yellowish-white powder, which can be rendered soluble only by fusion with potassium bisulphate.

Cerium Carbide.—Produced by heating cerous formate or oxalate in a closed crucible completely filled with it, or better in a glass tube through which a stream of hydrogen is passed. A black-grey powder then remains, which while hot burns like tinder on exposure to the air, but remains unaltered if kept from contact with the air. Hydrochloric acid extracts from it a certain quantity of cerous oxide, leaving the carbide in the form of a dense black powder insoluble in concentrated acids even when heated, and agreeing approximately in composition with the formula CeC^4 (Delafontaine, *Jahresb.* 1865, p. 177).

Cerous Chloride. $CeCl^2$.—By digesting ceroso-ceric oxide with hydrochloric acid and hydroferrocyanic acid, colourless crystals of hydrated cerous chloride are obtained having the composition $2CeCl^2.9H^2O$ (Lange, *J. pr. Chem.* lxxxii. 129). The *platinochloride* (i. 833) is crystalline and contains $2CeCl^2.PtCl^4.8H^2O$. The *aurochloride* $3CeCl^2.2AuCl^3.20H^2O$ is obtained—by leaving a mixture of the concentrated solutions of cerous chloride and auric chloride for several days over calcium chloride, and recrystallising several times—in yellow, transparent, apparently monoclinic crystals, which deliquesce rapidly in the air, but effloresce over caustic potash, melt in their water of crystallisation at a temperature considerably below 100°, and are soluble in absolute alcohol (Holzmann, *Zeitschr. Ch. Pharm.* 1862, p. 668).

A *chloro-iodide of cerium and zinc* is obtained, as a viscid syrup, or sometimes in crystals, by leaving a mixture of cerous chloride and zinc iodide to stand over quicklime and calcium chloride. The crystals are very soluble in water and in alcohol, and are decomposed by heat (Holzmann, *Jahresb.* 1861, p. 189).

Cerous Iodide. CeI^2.—Dry ceroso-ceric oxide dissolves easily in aqueous hydriodic acid, with elimination of iodine; and if the free iodine be reconverted into hydriodic acid by a current of hydrogen sulphide, and the solution evaporated in an atmosphere of that gas, a colourless liquid is obtained, which when left over sulphuric acid deposits the iodide in transparent colourless crystals, which deliquesce in the air to a brown liquid (Lange, *J. pr. Chem.* lxxxii. 129).

Oxides.—*Ceroso-ceric oxide*, Ce^3O^4, is obtained in crystals belonging to the regular system, mostly cubo-octohedrons, by heating cerous chloride with borax for 48 hours in a porcelain furnace, and treating the fused mass with hydrochloric acid. A heavy powder is then left, consisting of transparent colourless crystals of sp. gr. 6·94 at 15°, insoluble in hydrochloric acid, sparingly soluble in sulphuric acid. In one experiment brick-red crystals were obtained having a sp. gr. of 7·09 at 14·5° (Nordenskiold, *Pogg. Ann.* cxiv. 612).

According to Hermann (*J. pr. Chem.* xcii. 113; *Jahresb.* 1864, p. 193), the oxide produced by calcining cerous oxalate with free access of air, or by igniting ceroso-ceric sulphate with 2 pts. sodium carbonate and lixiviating the residue, consists of ceric oxide Ce^2O^3; but this view of its composition is contrary to the results obtained by Rammelsberg, Marignac, Holzmann, and others (i. 834). Hermann further states that an oxide Ce^5O^8 or $2Ce^2O^3.CeO^2$ is formed by the calcination of cerous nitrate, or by heating the supposed sesquioxide in oxygen gas. According to Stapf (*J. pr. Chem.* lxxix. 257), the residue obtained by calcining cerous nitrate in an open vessel consists of the dioxide CeO^2, or perhaps of Ce^3O^7. According to Popp (*Ann. Ch. Pharm.* cxxxi. 36), the yellow precipitate formed on treating a solution of crude cerium oxide mixed with sodium acetate, with chlorine or hypochlorous acid (p. 419), is a hydrate of the dioxide; this statement however does not appear to be founded on any quantitative determination; moreover, the anhydrous oxide which Popp obtained by calcining the yellow hydrate in the air had a brown colour, indicating the presence of didymium.

Oxygen-salts.—On the sulphates and double nitrates of cerium, see Zschiesche (*J. pr. Chem.* cvii. 65; *Zeitschr. f. Chem.* [2] vi. 41).

Silicide. CeSi.—Ullik (*Zeitschr. f. Chem.* [2] ii. 60; *Jahresb.* 1865, p. 186), by subjecting a mixture of potassium fluoride and cerium fluoride fused in a porcelain crucible to the current of a battery of eight Bunsen's elements, obtained at the negative pole a brown mass mixed with globules of potassium. This mass triturated with water left a powder containing 23·19 p. c. silicon and 76·21 cerium, agreeing with the formula above given. The silicon was derived from the sides of the crucible, which were strongly attacked.

CEROTIC ACID. $C^{27}H^{54}O^2$.—This acid is produced, together with several of its lower homologues, by oxidising paraffin (melting at 66°) with potassium dichromate and sulphuric acid (adding a small quantity of manganese dioxide, which greatly facilitates the oxidation), or with nitric acid of sp. gr. 1·3 diluted with 1½ vol. water. The cerotic acid, purified by repeated crystallisation from alcohol and ether, melted at 78°, and was identical in all its characters with that obtained from Chinese wax (i. 837) (Gill a. Meusel, *Chem. Soc. J.* [2] vi. 466). According to Bérard (*Zeitschr. f. Chem.* [2] vi. 465), cerotic acid exists in the free state in carnaüba wax (p. 391), and may be extracted therefrom by alcohol.

CETANE or **CETYL HYDRIDE,** $C^{16}H^{34}$, is one of the constituents of American petroleum. When separated by fractional distillation it is a colourless liquid boiling at about 280°, and having a vapour-density of 8·078 (calc. 7·96) (Pelouze a. Cahours, *Compt. rend.* lvii. 62).

CETENE or **CETYLENE.** $C^{16}H^{32}$.—Bromine added by drops to cetene under water unites readily with it, forming cetene bromide, $C^{16}H^{32}Br^2$, a yellowish liquid which sinks in water and is decomposed by distillation even in a vacuum. By alcoholic potash it is converted into monobromocetene, $C^{16}H^{31}Br$, a yellowish liquid which floats on water. Cetene also unites with *chlorine*, but it is difficult to obtain definite compounds. *Cetene diacetate*, $C^{16}H^{32}(C^2H^3O^2)^2$, appears to be formed as a semifluid mass by heating the dibromide to 130°–140° with silver acetate and glacial acetic acid (Chydenius, *Ann. Ch. Pharm.* cxliii. 267).

Cetene Oxychloride or *Chlorohydrate*, $C^{16}H^{33}OCl = C^{16}H^{32}Cl(OH)$, the chlorhydrin of the unknown cetylic glycol, is obtained by agitating a well-cooled solution of hypochlorous acid (of at most 1 p. c., and still mixed with the mercuric oxychloride formed in its preparation) with cetene gradually added, till the acid is all decomposed. The resulting cetylic chlorhydrin is extracted by ether from the mercuric oxide with which it is mixed, and the colourless oil which remains on distilling off the ether, is freed from admixed mercuric chloride by agitation with solution of sal-ammoniac, and from unaltered cetene by prolonged heating to 250° in a stream of carbon dioxide. Pure cetene oxychloride distils at about 300° almost without decomposition; it becomes viscid, but not solid at −15°, and is resolved by potash into potassium chloride and cetene oxide, $C^{16}H^{32}O$, which crystallises in slender microscopic needles, melts at 30°, boils at 300°, and is insoluble in water (Carius, *Ann. Ch. Pharm.* cxxvi. 195).

CETINE. $C^{16}H^{30}$ (also called *Cetylene*).—This hydrocarbon, homologous with ethine or acetylene, is produced by distilling monobromocetene, $C^{16}H^{31}Br$, with sodium ethylate or calcium hydrate; also, together with oxalic acid, by heating an ethereal solution of cetene bromide with silver oxalate:

$$C^{16}H^{32}Br^2 + C^2Ag^2O^4 = C^{16}H^{30} + C^2H^2O^4 + 2AgBr.$$

It is a colourless liquid, lighter than water; boils without decomposition at 280°–285°; solidifies in a mixture of solid carbon dioxide and ether; becomes liquid again at −25°; dissolves easily in alcohol and ether. It unites with 2 at. bromine, forming a heavy yellow liquid which is easily decomposed by alcoholic potash, yielding potassium bromide and a dark-coloured liquid containing bromine. This latter, when quite freed from bromine, is a colourless hydrocarbon consisting for the most part of cetene boiling at 275° (Chydenius, *loc. cit.*).

CETYLIC ALCOHOL, $C^{16}H^{34}O$, is formed, together with octane, when sebic acid is heated with caustic baryta. The cetyl alcohol thus obtained melts at 49°, and solidifies again at the same temperature (Schorlemmer, *Proc. Roy. Soc.* xix. 22).

CETYLIC ALDEHYDE. Syn. with PALMITIC ALDEHYDE.

CHELIDONIC ACID. $C^7H^4O^6$ (i. 847).—The products of decomposition of this acid by heat and by bromine have been studied by J. Wilde (*Ann. Ch. Pharm.* cxxvii. 164; *Jahresb.* 1863, p. 388). At 150° it gives off water, in addition to that which is expelled at 100°; at 220° it softens, turns black, gives off carbon dioxide, and yields a crystalline sublimate melting at 55°. The aqueous solution of the residue leaves on evaporation a crystalline acid, to which Wilde assigns the formula $C^{15}H^{14}O^{14}$, its silver salt giving by analysis numbers approximating to the formula $C^{15}H^{12}Ag^2O^{14}$; but it is very improbable that an acid containing only 7 at. carbon and 4 at. hydrogen should be transformed by heat into another containing 15 at. C and 14 at. H. On treating an aqueous pulp of chelidonic acid with excess of *bromine*, and distilling the product with water, a heavy oil passes over, and a watery residue is left, together with an oil heavier than water. This latter solidifies on cooling to a crystalline mass, having the composition and properties of penta-bromacetone, CH^3Br^5O.

The watery liquid above this oil contains oxalic acid; and the oily distillate consists of bromoform. If this last compound be regarded as a secondary product, the action of bromine on chelidonic acid may be represented by the equation

$$C^7H^4O^6 + 5Br^2 + 3H^2O = C^3HBr^5O + 2C^2H^2O^4 + 5HBr.$$

Monoargentic chelidonate, $C^7H^3AgO^6.H^2O$, obtained by recrystallising the diargentic salt (i. 849) from very dilute nitric acid, forms white needles which give off their water at 140°–150° (Wilde).

CHEMICAL ACTION. Researches on the laws of connection between the conditions of a chemical change and its amount have been made by Harcourt a. Esson (*Proc. Roy. Soc.* xiv. 470; xv. 262; *Chem. Soc. J.* [2] v. 460). One of the reactions studied was that between *hydrogen dioxide* and *hydriodic acid* (or between a mixture of sodium or barium dioxide, hydrochloric acid, and potassium iodide). The progress of the reaction was observed by determining the intervals of time which elapsed between the successive appearances of the yellow coloration (or blue if starch was added) after the iodine, separated according to the equation

$$H^2O^2 + 2HI = 2H^2O + I^2,$$

had been recombined (reconverted into hydriodic acid) by addition of a small quantity of sodium hyposulphite. The solution of this salt was added by drops, and always in equal measures; and the amount of hyposulphite in such a measure, and the quantity of peroxide used, were accurately estimated. In this manner data were obtained for determining the quantity of hydrogen dioxide present in the mixture at the time t of a particular coloration, and the quantity y^1 still present at the time t^1 of the next coloration, whence the quantity $y-y^1$ of dioxide decomposed in the interval $t-t^1$ was determined. The observed results are given in the following table:

Amount of dioxide	Time from the beginning	Chemical change in each interval	Intervals
	′		
20·95	0·00		
19·95	4·57	1	4·57
18·95	9·37	1	4·80
17·95	14·5	1	5·13
16·95	19·87	1	5·37
15·95	25·57	1	5·70
14·95	31·68	1	6·11
13·95	38·20	1	6·52
12·95	45·23	1	7·03
11·95	52·82	1	7·59
10·95	61·12	1	8·30
9·95	70·15	1	9·03
8·95	80·08	1	9·93
7·95	91·27	1	11·19
6·95	103·88	1	12·61
5·95	118·50	1	14·62
4·95	135·85	1	17·35
3·95	157·00	1	21·15
2·95	181·53	1	27·53
1·95	223·45	1	38·92
0·95	291·13	1	66·73

The general conclusion deducible from these experiments is that the amount of change at any moment varies directly with the quantity of dioxide present in the solution; in accordance with this law, the quantities of dioxide at the end of a series of times taken in arithmetical progression are themselves in geometrical progression, and the curve which represents the relation between these times and quantities is a logarithmic curve.

These results are corroborated by experiments on the reaction between permanganates and oxalic acid in presence of sulphuric acid, the ultimate result of which is represented by the equation:

$$K^2Mn^2O^8 + 3H^2SO^4 + 5H^2C^2O^4 = K^2SO^4 + 2MnSO^4 + 10CO^2 + 8H^2O.$$

The observations were made by varying successively the quantities of sulphuric acid, permanganate, and oxalic acid, while the quantities of the other substances present remained constant.

The influence of the relative quantities of the reacting substances on the final result of a chemical action has been studied by Chiżyński (*Ann. Ch. Pharm. Suppl.* iv. 226; *Phil. Mag.* [4] xxxii. 388; *Jahresb.* 1866, 12) in the case of the action of phosphoric acid on mixed solutions of lime and magnesia. Solutions of calcium chloride and magnesium chloride were mixed with quantities of phosphoric acid sufficient only for partial precipitation, and with ammonia, and the proportion of the bases in the precipitate was determined. The composition of this precipitate, which invariably contained both lime and magnesia, was found to be nearly independent of the quantity of water used for dilution, and of the quantity of ammonia present, but to vary with the ratio between the calcium and magnesium salts, and with the proportion of both to the phosphoric acid. The results are given in the following table; 1 cub. cent. of the calcium chloride solution contained 28·5 milligr. lime; 1 c.c. of the magnesium chloride solution contained 21 milligr. magnesia; 1 c.c. of the phosphoric acid solution contained 72·3 milligr. phosphoric anhydride. The absolute quantity of phosphoric acid was in all the experiments 5 c.c.

Experimental liquid in c.c.		Contents of precipitate in		To 1 mol. P^2O^5 the precipitate contained mols. of		$\left(\frac{1}{x}\right)$	(x)
$CaCl^2$	$MgCl^2$	CaO	MgO	CaO	MgO		
10	10	0·2139	0·1376	1·50	1·35		
15	10	0·3182	0·1008	2·23	1·06		
20	10	0·3796	0·0758	2·66	0·74		
25	10	0·4073	0·0698	2·88	0·68		
30	10	0·4037	0·0515	2·83	0·50		
100	10	0·5159	0·0505	3·60	0·50		
15	10	0·3182	0·1008	2·23	1·00		
15	15	0·2727	0·1073	1·91	1·05		
15	20	0·2642	0·1244	1·85	1·22		
15	25	0·2449	0·1470	1·71	1·38		
15	30	0·1525	0·1542	1·07	1·51		
15	100	0·0289	0·2062	0·20	2·02		
10	10	0·2139	0·1376	1·50	1·35	$\frac{1}{0·928}$	0·928
15	15	0·2727	0·1073	1·91	1·05	$\frac{1}{0·733}$	0·733
15·6	15·6	0·3184	0·0860	2·25	0·85	$\frac{1}{0·616}$	0·616
19·5	19·5	0·3420	0·0800	2·40	0·78	$\frac{1}{0·573}$	0·573
25	25	0·3641	0·0978	2·55	0·96	$\frac{1}{0·613}$	0·613
50	50	0·4045	0·1156	2·83	1·11		
100	100	0·4302	0·1106	3·02	1·08		

These numbers lead to the following conclusions: When the two chlorides are mixed in equivalent proportions, the lime passes into the precipitate in greater equivalent proportion than the magnesia, and this proportion increases as the total quantity of the chlorides used is greater. When the quantity of calcium chloride is increased, that of the magnesium chloride remaining constant, the quantity of lime in the precipitate increases, while that of the magnesia diminishes; the contrary takes place when the quantity of calcium chloride remains constant, and that of the magnesium chloride increases; these variations in the composition of the precipitate are not sudden, but steady and gradual. With a large excess of calcium chloride the composition of the precipitate approximates to the formula $4RO.P^2O^5$; with excess of magnesium chloride to the formula $2RO.P^2O^5$, probably because the salt $Ca^4P^2O^9$ is produced in the former case, and $(NH^4)MgPO^4$ in the latter. It appears from this that the affinity of lime for phosphoric acid is greater than that of magnesia. On the other hand, from 2·5 to 3 mol. magnesium chloride, ($MgCl^2$), exert towards 1 mol. phosphoric acid the same action as 1·5 mol. calcium chloride, ($CaCl^2$), inasmuch as with these proportions in the solution, the two bases combine with the phosphoric acid in nearly equivalent proportions. The chemical action of a body is therefore a function of its chemical affinity and of its mass conjointly, increasing as the product of these magnitudes increases, though not in exact proportion thereto. Moreover, when the quantities of two bodies increase in equal proportion compared with a third for which they both have affinity, the chemical action of the body with the greater affinity increases more quickly, and that of the body with the smaller affinity decreases more quickly than might be expected according to their relative masses. The action of calcium chloride on phosphoric acid is always greater, and that of magnesium chloride is always less than they should be according to Berthollet's law of the action of masses (i. 860). To estimate the amount of chemical action according to quantity, it is necessary to multiply the chemical mass (the number of equivalents) with a *coefficient of affinity*, which varies with the mass, and, according to the preceding experiments, is, for calcium chloride, greater than unity $\left(\frac{1}{x} \text{ of } x < 1\right)$, and for magnesium chloride less than unity (x). Generalising this result, Chiżyński modifies Berthollet's law of the action of masses as follows: *Chemical actions* (W, W′) *are proportional to the products of the chemical masses* (M, M′) *and their coefficients of affinity*, $\left(\frac{1}{x} \; ; \; x\right)$, or:

$$W : W' = M\frac{1}{x} : M'x.$$

He calculated the coefficients of affinity for calcium chloride and magnesium chloride, taking account of the disturbing influence arising from the presence of sal-ammoniac and ammonia in the solutions, on the assumption that, with the smallest possible and equal chemical masses, their actions are proportional to these masses, and therefore equal; and finds that with equal increase of the chemical masses, the coefficient enters as a factor in the one case directly, in the other inversely, as appears from the values in the last column of the table, which agree nearly with the actual results of experiment. Equal masses of calcium chloride and magnesium chloride appear therefore to possess coefficients of affinity equal in magnitude, but opposite in direction. Chiżyński regards it as probable that the same law with regard to equal chemical masses of unequal chemical energy is universally applicable.

That reciprocal decomposition does not always take place between mixed salts as required by Berthollet's law, is shown by the following experiment of Bettendorff (*Zeitschr. f. Chem.* [2] ii. 641; *Jahresb.* 1866, 10). A solution of ferric acetate when examined by the spectroscope absorbs part of the spectrum (in the red and green, and especially in the violet), but does not exhibit any bands. If, however, a tube filled with vapour of nitrogen tetroxide be interposed between this solution and the source of light, bands make their appearance in numbers increasing with the strength of the solution. A very dilute solution of ferric chloride, either alone or mixed with ferric acetate, makes no alteration in the absorption spectrum of the latter, or in that of nitrogen tetroxide; the same is the case with potassium acetate. Now a solution of ferric acetate (containing from 0·0044 to 0·0350 grm. of the neutral salt in 26 c.c.), after addition of an equivalent quantity of potassium chloride, affects the spectrum of nitrogen tetroxide in exactly the same manner as an equally diluted solution of pure ferric acetate; and, moreover, a solution of ferric chloride mixed with an equivalent quantity of potassium acetate affects the said spectrum in exactly the same manner as an equally diluted solution of the entire quantity of ferric acetate corresponding to the ferric chloride; hence it must be inferred that potassium chloride and ferric acetate do not decompose one another, and that the reaction between potassium acetate and ferric chloride gives rise, not to four salts, but only to two—namely, potassium chloride and ferric acetate. For this reaction, therefore, Berthollet's law does not hold good.

Experiments on the degree of neutralisation of acids by different bases, and the modifications produced therein by the presence of neutral salts, have been made by Löwenthal a. Lenssen (*J. pr. Chem.* lxxxv. 241, 401; *Jahresb.* 1863, 120).

Influence of Pressure on Chemical Action.

When a body is decomposed by heat in a confined space, and one or more of the separated elements (ultimate or proximate) is gaseous, the decomposition goes on until the liberated gas or vapour has attained a certain tension greater or less according to the temperature. So long as this temperature remains constant no further decomposition takes place, neither do any portions of the separated elements recombine; but if the temperature be raised, decomposition recommences and goes on till the liberated gas or vapour has attained a certain higher tension, also definite for that particular temperature; if on the other hand the temperature be lowered, recomposition takes place, until the tension of the remaining gas is reduced to that which corresponds to the lower temperature. These phenomena, which are closely analogous to those exhibited in the vaporisation of liquids (iii. 81), have been especially studied by Deville (*Compt. rend.* xlv. 857; lvi. 195, 322; lx. 317, 884; *Jahresb.* 1857, 58; 1863, 27; 1865, 59, 63; *Leçons sur la Dissociation*, Paris, 1864) and Debray (*Compt. rend.* lxiv. 603; lxvi. 194; *Jahresb.* 1867, 85; 1868, 75). Deville designates decomposition under these conditions by the term 'Dissociation'; but the utility of this new word is by no means obvious.

1. When *calcium carbonate* is heated in an iron tube from which the air has been exhausted by means of a mercury-pump, no decomposition takes place at 300°, and a scarcely perceptible decomposition at 440°; but at 800° (in vapour of cadmium) it becomes very perceptible, and goes on till the tension of the evolved carbon dioxide becomes equivalent to 85 millimetres of mercury; there it stops so long as the temperature remains constant; but on raising the temperature to 1040° (in vapour of zinc) more carbon dioxide is evolved until a tension equivalent to about 520 mm. is attained. If the tension be reduced by working the pump, it is soon restored to its former value by a fresh evolution of carbon dioxide. If, on the other hand, the apparatus be allowed to cool, the carbon dioxide is gradually reabsorbed by the quicklime, and a vacuum is re-established in the apparatus.

2. Similar phenomena are exhibited in the *efflorescence of hydrated salts*. When such a salt is enclosed in a sealed and exhausted glass tube, also containing a small mercurial pressure-gauge, and heated to a constant temperature in a water-bath, the tension of the vapour emitted by it in the closed space is found to increase with the temperature, and to be constant for each particular temperature. As the temperature falls the tension diminishes, in consequence of the reabsorption of a portion of the aqueous vapour.

The efflorescence or hydratation of a salt exposed to the open air is determined by similar conditions. For as the pressure of the air has no perceptible influence on the tension of vapours which form in it, a salt will effloresce when the tension of its vapour is greater than that of the aqueous vapour in the atmosphere at the existing temperature; on the other hand, an effloresced salt will take up water from the air, if the tension of the vapour in the atmosphere is greater than that of the vapour which the effloresced salt emits at the same temperature.

In the decomposition of calcium carbonate by heat, the maximum tension of the evolved gas corresponding to each particular temperature is quite independent of the proportion of the compound already decomposed; and the same is the case in some instances of the efflorescence of salts, but not in all. Take for example the common disodic phosphate $Na^2HPO^4 + 12H^2O$. The tension of the vapour emitted by this salt is at first independent of its state of efflorescence. Thus a salt containing all its water (62·8 p. c.) and an effloresced salt containing only 53 to 54 p. c., emit vapours of exactly the same tension at any given temperature; but when the quantity of water is reduced to 50 p. c., corresponding to the hydrate $Na^2HPO^4 + 7H^2O$ (which is obtained by crystallising the salt below 31°), the tension of its vapour is much less. On comparing the tensions of the vapour emitted by a salt containing 49·5 p. c. water with that emitted by the salt containing $12H^2O$, the following differences have been observed:

Temperature	Na^2HPO^4 with 7 to 12 aq. mm.	Na^2HPO^4 with rather less than 7 aq. mm.
12·3°	7·4	4·8
16·3	9·9	6·9
20·7	14·1	9·4
24·9	18·2	12·9
31·5	30·2	21·3
36·4 (melting point)	39·5	30·5
40·0	50·0	41·2

Hence it appears that, in its first phase of decomposition, ordinary sodium phosphate behaves like a compound of water with the hepta-hydrated salt. This compound decomposes just like calcium carbonate, emitting aqueous vapour whose tension is constant for a given temperature, whatever may be the proportion of water and hepta-hydrated phosphate existing in the effloresced salt; but when this first phase is terminated, and the quantity of water in the residue is reduced to 7 molecules, this hepta-hydrated salt likewise gives off aqueous vapour, but of lower tension for a given temperature. The difference between the decomposition of hydrated salts by heat, and that of calcium carbonate, consists therefore in this, that there are no compounds intermediate between calcium oxide and calcium carbonate, as there are between an anhydrous salt and its highest hydrate. A careful study of the vapour-tensions of hydrated salts would afford the means of determining the several hydrates which the same salt is capable of forming (Debray).

3. Similar phenomena are exhibited by certain compounds of *ammonia* with *metallic chlorides*. The compound $AgCl.3NH^3$, formed by exposing well-dried silver chloride to ammonia gas at 0°, possesses sufficient tension at ordinary temperatures to render it possible to remove half the ammonia by exhaustion with the air-pump, so as to convert the compound into $2AgCl.3NH^3$. The tension of the latter at 68° is 760 mm.; that of the compound $AgCl.3NH^3$ at 20° is 800 mm.; at these temperatures therefore the compounds in question cannot be formed under the ordinary atmospheric pressure. Both of them when heated in a Faraday's tube yield liquid ammonia; if the cooled arm of the tube has a temperature of about 13·5°, the compound $AgCl.3NH^3$ must be heated to 56°, the compound $2AgCl.3NH^3$ to 103°, at which it melts. *Iodide* and *cyanide of silver* take up but small quantities of ammonia, forming compounds which behave in a similar manner to the ammoniacal compounds of silver chloride (Isambert, *Compt. rend.* lxvi. 1259; *Jahresb.* 1868, 182).

Calcium chloride forms with ammonia the compounds $CaCl^2.2NH^3$; $CaCl^2.4NH^3$; $CaCl^2.8NH^3$. The two latter at given temperatures give off ammonia of constant tension, this tension increasing, as in the preceding case, as the temperature rises. When half the ammonia has been expelled from the compound $CaCl^2.8NH^3$, the tension suddenly falls to that which corresponds to the compound $CaCl^2.4NH^3$. The compound $CaCl^2.2NH^3$ is decomposed with difficulty, and only at high temperatures. Similar relations are exhibited by the compounds $CaI^2.6NH^3$; $ZnCl^2.6NH^3$; and $MgCl^2.6NH^3$, the two latter being converted by heat into $ZnCl^2.4NH^3$ and $MgCl^2.4NH^3$ respectively; also by the mercurous compound $Hg^2Cl^2.2NH^3$ (Isambert).

4. We have next to consider decompositions in which the decomposed body, as well as one at least of its constituents, is gaseous. In these cases it is not possible to obtain an exact measurement of the maximum tension corresponding to the temperature; nevertheless the decomposition is found to take place according to the same general law, ceasing as soon as the liberated gases have attained a certain tension, which is greater as the temperature is higher.

It has long been known that chemical combination between any two bodies capable of uniting directly takes place only at and above a certain temperature, and that the combination is broken up at a higher temperature; but it is only in later years that we have become acquainted with the fact that bodies like water begin to decompose at temperatures considerably below that which they produce in the act of combining, and therefore that their combination at that temperature is never complete. Grove showed some years ago that *water* is resolved into its elements in contact with intensely ignited platinum. This reaction has been more closely studied by Deville, who finds that when vapour of water is passed through a heated platinum tube, decomposition commences at 960°–1000° (about the melting point of silver), but proceeds only to a limited extent; on raising the temperature to 1200°, further decomposition takes place, but again only to a limited amount, ceasing in fact as soon as the liberated oxygen and hydrogen have attained a certain higher tension. The quantity of these gases actually collected in this experiment is however very small, the greater portion of them recombining as they pass through the cooler part of the apparatus, till the tension of the remainder is reduced to that which corresponds to the lower temperature. In Grove's experiment, the heated platinum first becomes surrounded with an atmosphere of aqueous vapour, part of which is then resolved into oxygen and hydrogen; but these gases as they rise to the surface are cooled by the water, and therefore recombine as above. The recombination of the mixed gases is not however quite complete, because they are surrounded by a considerable excess of aqueous vapour, which interferes with their combustion. (See next page.)

The recombination of the gases may be prevented to a greater extent by means of an apparatus consisting of a wide tube of glazed earthenware, through the axis of which passes a narrower tube of porous earthenware, the two being tightly fitted by perforated corks provided with gas-delivery tubes, and the whole strongly heated by a furnace. Vapour of water is passed through the inner tube, carbon dioxide through the annular space between the two, and the gases, after passing through the heated tubes, are received over caustic potash-solution. The vapour of water is then decomposed by the heat as before; but the hydrogen, according to the laws of diffusion, passes through the porous earthenware into the surrounding atmosphere of carbon dioxide, being thus separated from the oxygen, which remains in the inner tube, and becomes mixed with carbon dioxide passing through the porous septum in the opposite direction to the hydrogen. As these gases pass through the alkaline water, the carbon dioxide is absorbed, and a mixture of hydrogen and oxygen collects in the receiver. A gramme of water passed in the state of vapour through such an apparatus yields about a cubic centimetre of detonating gas (Deville).

A small quantity of water is likewise decomposed when a stream of carbon dioxide saturated with aqueous vapour is passed through an intensely heated porcelain tube filled with fragments of porcelain. The gaseous mixture, collected over potash, exhibited in two experiments the following composition:

Oxygen	46·1	46·8
Hydrogen	35·4	31·9
Carbon monoxide	12·0	10·7
Nitrogen	6·5	10·6
	100·0	100·0

The carbon monoxide arises from the reducing action of the hydrogen on the carbon dioxide; the nitrogen is an accidental admixture. The quantity of detonating gas obtained in this experiment is only about a fourth of that in the preceding, because the separated oxygen and hydrogen remain in contact during the cooling of the mixture; their complete recombination is however prevented by diffusion through a large quantity of neutral gas, just as the detonation of a mixture of the same or other combustible gases by the electric spark is prevented by the presence of a large excess of either of them, or of any indifferent gas. In like manner, in Grove's original experiment of the decomposition of water by incandescent platinum, the complete recombination of the gases is prevented by their diffusion through a considerable quantity of aqueous vapour.

The decomposition of water at comparatively low temperatures may also be effected by passing its vapour over melted silver, hydrogen being then set free, and the oxygen being absorbed by the silver, which then acquires the property of spitting. In this experiment, first made by Regnault, the water is not decomposed by the superior affinity of the silver for oxygen, for silver does not oxidise at that temperature; but the decomposition of the water, as in the former cases, is a direct effect of heat, and the oxygen thereby liberated does not combine with the silver, but is simply absorbed by it. That such is the case, Deville has shown by substituting litharge for the silver. When vapour of water is passed over litharge contained in a platinum boat, placed within a porcelain tube and heated to 1200°–1300°, the litharge remaining in the boat after the experiment is found to have absorbed oxygen, which has subsequently escaped from it by spitting, and part of the litharge carried over in fine particles by the vapour has been reduced to metallic lead, forming a black ring at that part of the tube where the heat, though rather high, was not great enough to melt the litharge. These results show that part of the aqueous vapour had been resolved into oxygen and hydrogen.

5. *Carbon dioxide* passed through a porcelain tube filled with fragments of porcelain, and heated in a furnace to 1200°–1300°, is partly resolved into carbon monoxide and free oxygen. In one experiment the gaseous mixture received over potash was found to consist of 30 p. c. oxygen, 62·3 carbon monoxide, and 7·7 nitrogen.

6. When *carbon monoxide* is passed through an intensely heated porcelain tube in the axis of which is fixed a narrow tube of silvered brass, and a stream of water cooled to 10° is passed through the metal tube during the whole of the experiment, the surface of this tube becomes coated at its lower part with a black layer of carbon. The particles of the carbon monoxide in contact with the lower part of the porcelain become strongly heated, and consequently expand and rise, striking against the lower surface of the metal tube; at the same time they are decomposed, and their carbon is deposited on the cold surface of the metal; if the tube were not kept cool, the carbon thus set free would recombine with the oxygen.

7. *Sulphurous oxide* may be decomposed in a precisely similar manner, the metal tube, however, having a thicker coating of silver than in the preceding case. The sulphurous oxide is resolved into oxygen and sulphur, the latter uniting with the silver (sulphurous oxide itself does not attack silver even at 300°), while the oxygen combines with another portion of sulphurous oxide, converting it into sulphuric oxide or anhydride, which is deposited in white flocks on the cooled surface.

8. When dry *hydrochloric acid gas* is passed through the same apparatus, the surface of the metal tube having been previously slightly amalgamated, decomposition takes place to a small extent at about 1300°, a small quantity of hydrogen gas being

given off, and small quantities of mercurous chloride and silver chloride being formed on the surface of the metal tube.

Carbon dioxide, sulphur dioxide, and hydrochloric acid gases are decomposed by a stream of induction-sparks nearly in the same way as by heat in the apparatus just described. In fact the decomposing action of the electric spark appears to be due merely to the great heat which it evolves. The particles in the immediate neighbourhood of the spark, and these alone, become intensely heated and are decomposed, the separated elements being immediately diffused through a large mass of the undecomposed gas and thereby cooled—as by the cold metal tube in the experiments above described—below the temperature at which they can recombine.

On the decomposition of *hydriodic acid* by heat, see Iodine; on that of *cyanuric acid*, see Cyanic Acid.

The influence of pressure on chemical decomposition is seen in other reactions besides those which are brought about by heat. Babinet in 1828 (*Ann. Ch. Phys.* [2] xxxvii. 183) found that zinc and dilute sulphuric acid cease to give off hydrogen when the pressure of this gas amounts to thirteen atmospheres at 10°, or to thirty-three atmospheres at 25°. Faraday had previously observed that under these circumstances the evolution of gas is not arrested, but only retarded (*New Quarterly Journal of Science*, iii. 474); and the same result appears to follow from the experiments of L. Gmelin.

Lothar Meyer (*Pogg. Ann.* civ. 189; *Phil. Mag.* [4] xvi. 160) found, by experiments in which, as in those of Gmelin, zinc and sulphuric acid were enclosed together in sealed glass tubes, that, with acid of the most various strengths, even in presence of large quantities of metallic sulphates, and likewise when citric and acetic acids were used, the pressure of the eliminated hydrogen very greatly exceeded the limits assigned by Babinet (amounting to sixty-six atmospheres at 0°). Nevertheless, the chemical action under these circumstances appeared to reach a limit, inasmuch as the liquid, after remaining in the tube for several months, even in contact with excess of zinc, still exhibited a very strong acid reaction. According to Favre (*Compt. rend.* li. 827), the decomposition of dilute sulphuric acid by zinc still goes on under a pressure of eighty-six atmospheres, but at a slower rate.

Similar observations have been made by Cailletet (*Compt. rend.* lxviii. 395; *Zeitschr. f. Chem.* [2] v. 190) on the action of hydrochloric acid upon zinc. A plate of zinc which, when acted upon by hydrochloric acid in the open air, exhibited after a certain time a loss of weight denoted by 10, suffered, under precisely similar circumstances, excepting that the materials were exposed to a pressure of 60 atmospheres, a loss of only 4·7, and under 120 atmospheres only 0·1. In like manner the quantities of calcium carbonate dissolved by nitric acid in the same time under a pressure of 150 atmospheres, and in the open air, were found to be as 1 to 11·09. A similar retardation of chemical action under pressure takes place in many other instances. The electrolysis of water is retarded under pressure. The action of sodium-amalgam on water in sealed glass tubes is entirely or almost entirely arrested as soon as the evolved hydrogen has attained a certain tension. Chemical action thus retarded by pressure may be accelerated again by rise of temperature. The quantities of gas evolved by the action of dilute sulphuric acid on a plate of zinc in a sealed tube at 0° and at 50° were to one another as 1 to 2·8. Under diminished pressure the preceding reactions go on with increased rapidity, the quantity of metal dissolved in an acid in a given time being greater in a vacuum than under ordinary pressure. With aluminium in hydrochloric acid the ratio is 1 : 1·68; with zinc in sulphuric acid 1 : 1·53; with calcium carbonate in nitric acid, 1 : 2·51.

From the preceding results Cailletet concludes that, under a certain pressure, substances which ordinarily react on one another become actually indifferent. Berthelot, on the other hand (*Zeitschr. f. Chem.* [2] v. 191), maintains that the action of acids upon metals under the circumstances above described is not completely arrested, but only retarded, the retardation arising partly from the formation of a film of saturated solution at the surface of the metal, partly from the adhesion of hydrogen to its surface. Under increased pressure, the gas-bubbles become smaller and move less freely, and consequently the agitation of the liquid, which under ordinary atmospheric pressure is caused by these gas-bubbles and facilitates the transport of fresh acid to the surface of the metal, is greatly impeded: hence the retardation. To these observations Cailletet replies (*ibid.* 368) that he has kept zinc and sulphuric acid for twelve days in sealed tubes, which were continually agitated by a mechanical arrangement, and that on opening the tubes the acid was found to be still unsaturated, and capable again of acting on the zinc under ordinary pressure.

In all the reactions above noticed, the elimination of a gas is an essential condition of the change, and this being prevented, the action is retarded. On the other hand, there are numerous reactions which are greatly promoted by increased pressure—those, namely, which depend on the solution of gases in liquids, or on the prolonged contact of substances which under ordinary pressure would be volatilised by heat. Beketoff has shown (*Compt. rend.* xlviii. 442; *Zeitschr. f. Chem.* 1865, 376; *Jahresb.* 1859, 66; 1865, 13) that solutions of silver nitrate and sulphate, and an ammoniacal solution of silver chloride, are reduced by hydrogen in sealed tubes, though under the ordinary atmospheric pressure, little or no reduction takes place; dilute solutions of silver sulphate are reduced under lower pressures than concentrated solutions. A solution of calcium acetate is decomposed by carbon dioxide under a pressure of twenty-seven to twenty-eight atmospheres, calcium carbonate being precipitated in microscopic spherical groups of pointed crystals; under fourteen atmospheres no precipitation takes place. Carbon dioxide does not decompose a neutral solution of calcium of chloride under a pressure of forty-five atmospheres, or of barium chloride at forty, or of barium acetate at thirty atmospheres.

Theories of Chemical Action and Chemical Affinity, and of the Constitution of Chemical Compounds, have been proposed by:

Czirmanski, *Theorie der chemischen Verbindungen auf die rotirende Bewegung der Atome basirt.* Krakau, 1863 and 1865. *Jahresb.* 1863, 8; 1868, 6.

Maumené, *Ann. Ch. Phys.* [4] iii. 319; *Bull. Soc. Chim.* [2] ii. 129; *Jahresb.* 1864, 8; further, *Compt. rend.* lxii. 697; *Jahresb.* 1866, 9.

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CHENEVIXITE. A ferruginous cupric arsenate from Cornwall, occurring in quartz-rock, as a dark green compact mass, of sp. gr. 3·93 (nearly), and hardness 4·5. Gives by analysis 32·20 p. c. As^2O^5, 2·30 P^2O^5, 31·70 CuO, 25·10 Fe^2O^3, 0·34 CaO, and 8·66 water (= 100·30) (Pisani, *Bull. Soc. Chim.* [2] vi. 30).

CHENOPODINE. $C^6H^{13}NO^4$.—A base existing in white goosefoot (*Chenopodium album*), and produced in small quantity in the putrefaction of yeast and of vegetable juices. It is prepared by heating the recently expressed juice of the young plant, to free it from albumin, then evaporating to a thin syrup, treating the extract with hot alcohol, and again evaporating the alcoholic solution. The chenopodine, which gradually separates in grains, is pressed, washed with ether, and then dissolved in alcohol of 80 p. c., from which it separates in the pure state on cooling. It is a white, granular, tasteless, and inodorous powder, appearing under the microscope as a mass of spherules made up of concentric needles, and when moistened with amyl alcohol or linseed-oil varnish, exhibiting a dark cross in polarised light. It dissolves in 3 to 4 pts. of hot and about 11 pts. of cold water; in 77 pts. of boiling and 200 pts. of cold alcohol. At 200° it begins to sublime in snow-white crystals, and at 225° sublimes completely, becomes liquid, and begins to boil, giving off an extremely pungent repulsive odour. Melting sodium hydrate converts it, with evolution of ammonia, into a peculiar acid. On adding bromine to the alcoholic solution, a red powder separates after a while, and the red solution deposits large cubic crystals of *chenopodine hydrobromide*. The *hydrochloride* likewise crystallises in cubes, and forms a yellow precipitate with platinic chloride. The *sulphate* and *nitrate* crystallise in rhombic needles (H. Reinsch, *N. Jahrb. Pharm.* xx. 268; xxi. 132; xxvii. 193; *Jahresb.* 1863, p. 613; 1867, p. 531; also *Wittstein's Vierteljahrsschrift*, xvii. 37; *Zeitschr. f. Chem.* [2] iv. 670).

CHIASTOLITE occurs near Lancaster in Massachusetts, in large elongated nodules an inch thick, and exhibiting a well-marked crucial structure in the interior. Sp. gr. 2·923. Composition 41·95 SiO^2, 48·60 Al^2O^3, 9·30 Fe^2O^3, 0·41 CaO (= 100·26) (Petersen, *Jahresb.* 1860, p. 925).

CHILDRENITE. This mineral occurs, with amblygonite, at Hebron in Maine (U.S.), forming small hair-brown crystals essentially similar in form to those found at Tavistock in Devonshire (i. 869), but distinguished by the occurrence of the face oP, and prismatically elongated in the direction of the brachydiagonal. Combination $oP . P . 2\breve{P}\infty . \infty\breve{P}\infty$ (G. J. Brush, *Sill. Am. J.* [2] xxxvi. 257. J. P. Cooke, *ibid.* 258).

CHIMAPHYLLIN. A yellow crystalline substance obtained from *Pyrola* (or *Chimaphylla*) *umbellata* (iv. 760).

CHINOLINE. C^9H^7N.—This base, like aniline (iv. 429, 475), unites with metallic salts, forming compounds represented by the general formula $C^9H^7N . MX$, where M denotes a metal (univalent), and X an acid radicle. These compounds are mostly crystallisable, slightly soluble in cold water, decomposed by the prolonged action of boiling water, and turn slightly yellow when exposed to sunlight. The *zinc-compound* $(C^9H^7N)^2 . ZnCl^2$ crystallises from a hot solution in small prisms, apparently monoclinic. The *mercury-compound* $(C^9H^7N)^2Hg(NO^3)^2$ is a white precipitate nearly insoluble in pure water, but crystallisable from very dilute nitric acid. By decomposing the corresponding acetate with various salts of the alkali-metals, the more easily decomposible compounds of chinoline with other mercury salts may be prepared. A compound of chinoline with *mercuric cyanide*, $(C^9H^7N)^2 . HgCy^2$, crystallises from water in long shining prisms. Chinoline unites in like manner with stannic chloride, bismuth chloride, antimonious chloride, and arsenious chloride; but the resulting compounds are less stable than the corresponding salts of aniline. Acids decompose the compounds of chinoline with metallic salts (except the mercury-compound), giving rise to crystallisable double salts, of which the following are examples:

Antimony salt	$SbCl^3 . C^9H^8NCl$
Zinc salt	$ZnCl^2 . 2C^9H^8NCl$
Stannic salt	$SnCl^4 . 2C^9H^8NCl$
Bismuth salt	$BiCl^3 . 3C^9H^8NCl$

(H. Schiff, *Ann. Ch. Pharm.* cxxxi. 112; *Jahresb.* 1863, p. 429).

Tribromochinoline, $C^9H^4Br^3N$, is produced by the action of bromine-vapour on chinoline, and crystallises from alcohol in colourless silky needles, which melt at 173°–175°, and volatilise without residue at a higher temperature. Insoluble in water, sparingly soluble in cold, easily in hot alcohol, easily also in strong hydrochloric or sulphuric acid, and precipitated therefrom by water. When fused with potash it exhibits the same colours as chinoline. A compound intermediate between tri- and tetra-bromochinoline is formed by the action of bromine on chinoline-sulphuric acid (Lubavin, *Zeitschr. f. Chem.* [2] v. 690).

Chinoline-sulphuric acid, $C^9H^6N . SO^3H$, formed by heating chinoline for several days with fuming sulphuric acid, separates from hot water in large anhydrous crystals, easily soluble in alcohol, insoluble in ether. The *barium salt* $(C^9H^6NSO^3)^2Ba$ is sparingly soluble in water and separates on evaporation in warty crusts. The *silver salt* crystallises in sparingly soluble needles. The acid fused with potash gives off vapours of chinoline and leaves a black amorphous mass (Lubavin).

CHINOLINE-BLUE or **CYANINE.** The blue dye known in commerce by these names, which was discovered by C. Gr. Williams (i. 873), and is prepared on the large scale by Müller in Basel, has been investigated chemically by Nadler a. Merz (*J. pr. Chem.* c. 129; *Jahresb.* 1867, p. 512). It is an amyl-chinoline derivative having the composition $C^{28}H^{35}IN^2$, whereas the similarly named compound from the works of Ménier in Paris, examined by Hofmann, is an amyl-lepidine derivative, $C^{30}H^{39}IN^2$ (iii. 573).

Chinoline-iodocyanine, or more shortly *Iodocyanine*, $C^{28}H^{35}IN^2$, forms, accordingly as it is recrystallised by spontaneous evaporation or by cooling of very concentrated alcoholic solutions, cantharides-green prisms and scales, or crystalline grains of a brass-yellow to bronze-yellow colour, differing from one another by their amount of water. It is very slightly soluble in cold water and in ether; very soluble, with deep dark blue colour, in hot alcohol; and melts at 100°, with loss of water, to a bronze-coloured liquid which solidifies to a crystalline mass on cooling. Its formation by the action of potash on amylchinoline iodide (i. 873) is represented by the equation:

$$\underset{\substack{\text{Amyl-chinoline}\\\text{iodide.}}}{2C^9H^7(C^5H^{11})NI} + KHO = KI + H^2O + \underset{\substack{\text{Chinoline-iodo-}\\\text{cyanine.}}}{C^{28}H^{35}IN^2}$$

The colourless solution of chinoline-iodocyanine in hydrochloric acid deposits on evaporation colourless scales of the hydrochloride $C^{28}H^{35}IN^2 . 2HCl$, which in the exsiccator gradually crumble to a yellow powder; at 100° this salt gradually gives off half its hydrochloric acid, leaving the bronze-coloured salt $C^{28}H^{35}IN^2.HCl$, sparingly soluble in water, easily in alcohol.

Chinoline-cyanine, or more shortly ***Cyanine***, $C^{28}H^{36}N^2O$ or $C^{28}H^{35}(OH)N^2$, is obtained, together with resinous substances, by treating the iodine-compound with recently precipitated silver oxide, or with potash in alcoholic solution, as a viscid, uncrystallisable mass.

Chlorocyanine, $C^{28}H^{35}ClN^2$, is obtained by mixing the solution of cyanine in hydrochloric acid with ammonia, or by decomposing an acetic acid solution of sulphatocyanine (*infra*) with barium chloride, and saturating the filtrate with ammonia; or by digesting an alcoholic solution of iodocyanine with silver chloride. It forms brown flocks easily soluble in hot water and in alcohol, and separates from the former in a coherent cake of long blue prisms, from the latter by spontaneous evaporation, in cantharides-green shining needles, or in dark green prisms and tables. In the air-dried state it contains $4H^2O$ (14·2 p. c.). It dissolves without colour in acids, forming salts resembling those of iodo-cyanine.

Nitratocyanine, $C^{28}H^{35}(NO^3)N^2$, is obtained by precipitating an alcoholic solution of iodocyanine containing a little nitric acid, with silver nitrate, supersaturating the filtrate (freed from silver by cautious addition of hydrochloric acid) with excess of ammonia, and distilling off the alcohol. The residual resinous mass, which solidifies in the crystalline form, is purified by recrystallisation from very weak spirit. Nitratocyanine crystallises with 1 mol. (3·76 p. c.) water in bronze-coloured highly lustrous rhombic needles and prisms, sparingly soluble in ether and in cold water, more easily and with splendid blue colour in hot water and alcohol. The solution of nitratocyanine in hydrochloric acid deposits by evaporation over quicklime, long transparent prisms of the compound $C^{28}H^{35}N^3O^3.2HCl$, which when heated above 65°, gives off HCl, and is converted into the blue salt $C^{28}H^{35}N^3O^3.HCl$. Nitratocyanine heated with ammonium sulphide yields, together with other products, a slightly basic compound, dissolving with red colour in ether, and separating therefrom in shining yellowish-red monoclinic crystals, whose analysis leads to the formula $C^{56}H^{80}N^4S^2O^3$.

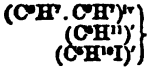
Sulphatocyanine, $C^{56}H^{70}(SO^4)''N^4.4H^2O$, is formed, with evolution of iodine and sulphurous oxide, on heating iodocyanine with excess of strong sulphuric acid:

$$2C^{28}H^{35}IN^2 + 2H^2SO^4 = C^{56}H^{70}(SO^4)N^4 + 2H^2O + I^2 + SO^2.$$

On diluting the acid solution with water and adding ammonia, the sulphatocyanine is precipitated in bulky red-brown flocks, and separates from a hot aqueous solution, like chlorocyanine, in a mass of long blue needles, resembling a blood-clot.

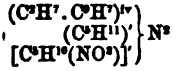
Cyanine-platinochloride, $C^{28}H^{36}N^2Cl^2.PtCl^4$ or $C^{28}H^{35}ClN^2.HCl.PtCl^4$, is formed as a yellow hydrated precipitate on adding platinic chloride to the hydrochloric acid solution of a cyanine salt.

Iodocyanine and its analogues may be regarded as diamines (sulphatocyanine as a tetramine), represented by the following formulæ:



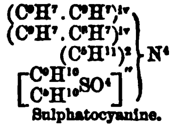
$$\left.\begin{array}{r}(C^9H^7.C^9H^7)^{iv}\\(C^5H^{11})'\\(C^5H^{10}I)'\end{array}\right\}N^2$$

Iodocyanine.



$$\left.\begin{array}{r}(C^9H^7.C^9H^7)^{iv}\\(C^5H^{11})'\\ {[C^5H^{10}(NO^3)]'}\end{array}\right\}N^2$$

Nitratocyanine.



$$\left.\begin{array}{r}(C^9H^7.C^9H^7)^{iv}\\(C^9H^7.C^9H^7)^{iv}\\(C^5H^{11})^2\\ \left[\begin{array}{l}C^5H^{10}\\C^5H^{10}\end{array}SO^4\right]''\end{array}\right\}N^4$$

Sulphatocyanine.

These diamines form mono-acid and bi-acid salts, the latter being colourless, and converted at a moderate heat into the mono-acid salts, which are coloured like the bases themselves. Even silk decomposes the colourless solutions of the bi-acid salts, setting acid free and acquiring a deep blue dye. Chinoline-blue, which appears of an equally beautiful lilac tint by lamplight, is unable to withstand the action of sunlight.

CHINOLINE, HOMOLOGUES OF. Bases obtained, together with chinoline, by distilling cinchonine or quinine with potassium hydrate. Chinoline and lepidine may be partly separated by fractional distillation, and afterwards more completely by fractional crystallisation of their platinum salts (i. 869); but for separating the bases of higher boiling point, the latter method is alone available. The higher portion of the crude distillate (boiling above 270°), freed from pyrrol and other impurities by heating its hydrochloric solution with a little nitric acid, and filtered to separate a resinous mass, gives with platinic chloride yellow precipitates, the first of which contain the bases of highest molecular weight. The names and formulæ of the known bases of the series are given in the following table:

Chinoline,	C^9H^7N.	Pentahiroline,	$C^{13}H^{15}N$.
Lepidine,	$C^{10}H^9N$.	Isoline,	$C^{14}H^{17}N$.
Dispoline,	$C^{11}H^{11}N$.	Ettidine,	$C^{15}H^{19}N$.
Tetrahiroline,	$C^{12}H^{13}N$.	Validine,	$C^{16}H^{21}N$.

Dispoline is contained in the fraction boiling between 282° and 304°, and forms a beautiful orange-coloured platinum salt. By the action of sodium on these bases a substance is obtained which dyes silk a splendid orange-red (C. Gr. Williams, *Laboratory*, i. 109).

CHLORACETENE. Syn. with chlorethylidene. See ETHYLIDENE.

CHLORAL. $C^2HCl^3O = CCl^3.COH$.—Produced by heating trichloracetal with sulphuric acid to 150° (Paterno, *Zeitschr. f. Chem.* [2] iv. 733).

Chloral is converted by strong *sulphuric acid* into insoluble chloral, or metachloral, $C^6H^3Cl^9O^3$, which is afterwards resolved into chloralide and chloroform, or the products of decomposition of the latter, hydrochloric acid and carbon dichloride (Städeler, *Ann. Ch. Pharm.* cvi. 253):

$$\underset{\text{Metachloral.}}{2C^6H^3Cl^9O^3} = \underset{\text{Chloralide.}}{2C^5H^2Cl^6O^3} + 2HCl + C^2Cl^4.$$

Chloral or metachloral distilled with strong *nitric acid*, or a mixture of nitric and sulphuric acid, yields chloropicrin, CCl^3NO^2 (Kekulé, *ibid.* 144).

Chloral mixed with an alcoholic solution of *sodium ethylate*, is converted into chloroform and ethyl formate. The reaction however takes place wholly between chloroform and alcohol; thus:

$$\underset{\text{Chloral.}}{C^2HCl^3O} + \underset{\text{Alcohol.}}{C^2H^6O} = \underset{\text{Chloroform.}}{CHCl^3} + \underset{\text{Ethyl formate.}}{CH(C^2H^5)O^2}$$

The same reaction is produced by alcoholic potash, but not by alcohol alone, although great heat is produced on mixing the two liquids. Besides the chief products above mentioned, there are also formed sodium formate, ethyl oxide, and a small quantity of a liquid having a higher boiling point, probably Kay's tribasic formic ether (Kekulé, *Ann. Ch. Pharm.* cxix. 187).

When chloral is mixed with *phosphorus pentachloride*, added by small portions, the mixture being gently warmed each time, ultimately boiled for some hours, and then mixed with water, an oil separates out, which when distilled yields pentachlorodimethyl or pentachlorethane, C^2HCl^5 or $CCl^3.CHCl^2$:

$$CHCl^3O + PCl^5 = POCl^3 + C^2HCl^5.$$

The same compound appears to have been obtained, though not pure, by Regnault, by the action of chlorine in sunshine on ethyl chloride and ethylene chloride (i. 533, 573) (Paterno, *Zeitschr. f. Chem.* [2] v. 245).

Chloral hydrate introduced under the skin is converted, on coming in contact with the alkali in the blood, into chloroform and formic acid:

$$C^2HCl^3O.H^2O = CHCl^3 + CH^2O^2.$$

The physiological action of chloroform thus generated within the circulation is different from that which it exerts when inhaled, producing deep sleep, but not insensibility to pain. The chloroform and formic acid are ultimately converted into chloride and formate of sodium (Liebreich; Personne, *Compt. rend.* Nov. 8, 1869).

The preparation of chloral hydrate has lately been the subject of considerable attention, but all the methods given are merely modifications of that already described (i. 881). Müller a. Paul pass a current of dry and pure chlorine into pure absolute alcohol for about 70 hours, till the contents of the flask are converted into a white crystalline mass (*Deut. Chem. Ges. Berlin.* No. 16, 1859). See also Thomsen (*Zeitschr. f. Chem.* [2] vi. 156; Roussin, *ibid.* 96; Personne, *Compt. rend.* Dec. 27, 1869). According to Thomsen, chloral hydrate boils at 115° under a pressure of 755 mm., and solidifies at 40·2°. According to Müller a. Paul, it is readily sublimable, and may be thus obtained as a snow-white crystalline powder.

On chloral hydrate and alcoholate, see also B. H. Paul (*Pharm. J. Trans.* [3] i. 631; *Chem. Soc. J.* [2] ix. 134).

CHLORHYDRINS. *Monochlorhydrin* is converted by sodium-amalgam into propylene glycol: $C^3H^7O^2Cl + H^2 = HCl + C^3H^8O^2$ (Lourenco, *Compt. rend.* lii. 1043; Buff, *Bull. Soc. Chim.* [2] x. 123). It unites directly with trimethylamine, when heated with it, forming the compound $N(CH^3)^3.C^3H^5(OH)^2Cl$, which crystallises in slender needles soluble in water. The solution mixed with auric chloride forms orange-yellow needles of the gold-salt $N(CH^3)^3.C^3H^5(OH)^2Cl.AuCl^3$ (V. Meyer, *Zeitschr. f. Chem.* [2] v. 439).

Dichlorhydrin, $C^3H^5(OH)Cl^2$, heated with potassium cyanide and alcohol to 100° in a closed vessel for 24 hours, is converted into dicyanhydrin, which when boiled with potash yields oxypyrotartaric acid, $C^5H^8O^5$:

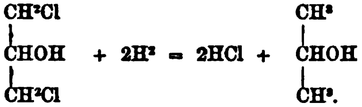
$$C^3H^6OCl^2 + 2KCN = 2KCl + C^3H^6O(CN)^2$$

and

$$C^3H^6O(CN)^2 + 2KHO + 2H^2O = 2NH^3 + C^5H^6K^2O^5$$

(Maxwell Simpson, *Proc. Roy. Soc.* xiii. 44).

Dichlorhydrin dissolved in ether free from alcohol, but not dehydrated, is converted by sodium-amalgam into isopropyl alcohol (Buff, *loc. cit.*):



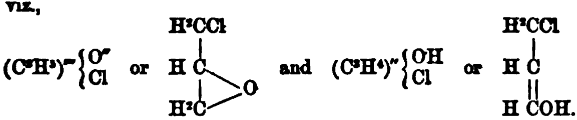
$$\begin{matrix} CH^2Cl \\ | \\ CHOH \\ | \\ CH^2Cl \end{matrix} + 2H^2 = 2HCl + \begin{matrix} CH^3 \\ | \\ CHOH \\ | \\ CH^3. \end{matrix}$$

Trichlorhydrin or *Glyceryl Trichloride*, $C^3H^5Cl^3$, is formed, together with other products, by the action of phosphorus pentachloride on acrolein. A convenient mode of preparing it is to heat acrolein hydrochloride, $C^3H^4O.HCl$, with 1 mol. phosphorus pentachloride as long as hydrochloric acid is given off, and submit the washed product to fractional distillation (Geuther, *Jahresb.* 1864, p. 333). It is also formed by the action of chlorine, or of a mixture of potassium chlorate and hypochlorous acid, on isopropyl iodide (Linnemann, *Jahresb.* 1865, p. 489). A solution of trichlorhydrin in 7 or 8 vol. alcohol, saturated with ammonia and heated to 130°–140° for three or four days, is converted into chlorodiallylamine (Engler, p. 95):

$$2C^3H^5Cl^3 + 5NH^3 = 4NH^4Cl + (C^3H^4Cl)^2NH.$$

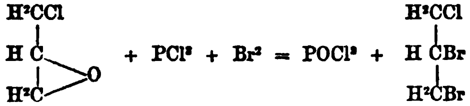
Respecting the chlorhydrins corresponding to propylphycite, see that compound.

Epichlorhydrin. C^3H^5OCl.—Two rational formulæ have been assigned to this compound, viz.,



$$(C^3H^5)'''\left\{\begin{matrix} O'' \\ Cl \end{matrix}\right. \text{ or } \begin{matrix} H^2CCl \\ | \\ H\,C \\ | \\ H^2C \end{matrix}\!\!>O \quad \text{and} \quad (C^3H^4)''\left\{\begin{matrix} OH \\ Cl \end{matrix}\right. \text{ or } \begin{matrix} H^2CCl \\ | \\ H\,C \\ \| \\ H\,COH. \end{matrix}$$

The first of these supposes that the oxygen is directly connected with two of the carbon-atoms; whereas the second supposes it to be joined to only one atom of carbon and to one atom of hydrogen—in other words, to be present as hydroxyl (ii. 896). That the former of these represents correctly the structure of epichlorhydrin is shown by the reaction of that compound with phosphorus trichloride and bromine. It appears indeed, from the experiments of Wichelhaus (*Ann. Ch. Pharm. Suppl.* vi. 277), that when organic bodies containing hydroxyl are thus treated, the ultimate products are a chlorinated organic compound, phosphorus oxychlorobromide, and hydrogen bromide, whereas bodies in which the oxygen is entirely combined with the carbon-atoms, like the ketones and oxides, yield as final products an organic bromide and phosphorus oxychloride. Now when epichlorhydrin is mixed with 1 mol. PCl^3 and 1 mol. bromine, (Br^2), is added by small portions to the cooled mixture, a product is formed which by repeated rectification may be separated into phosphorus oxychloride boiling at 110°, and dibromochlorhydrin, $C^3H^5Br^2Cl$ (i. 894), boiling between 195° and 200°:

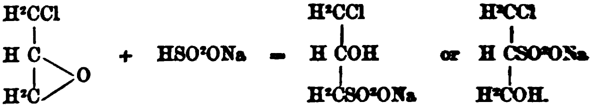


$$\begin{matrix} H^2CCl \\ | \\ H\,C \\ | \\ H^2C \end{matrix}\!\!>O + PCl^3 + Br^2 = POCl^3 + \begin{matrix} H^2CCl \\ | \\ H\,CBr \\ | \\ H^2CBr \end{matrix}$$

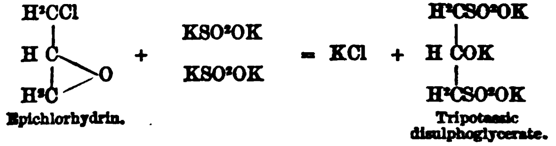
Epichlorhydrin. Dibromochlorhydrin.

If the epichlorhydrin molecule contained hydroxyl, the latter would be replaced by an atom of chlorine (Darmstädter, *Ann. Ch. Pharm.* clii. 319).

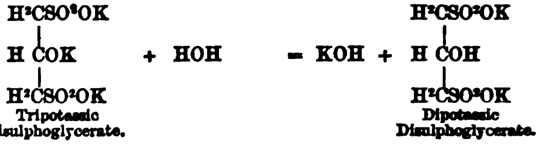
Epichlorhydrin heated to 100° with *acid sodium sulphite* unites with it directly, forming the beautifully crystallised sodium salt of chlormethyl-isethionic or chlorhydroxypropyl-sulphonic acid, $C^3H^4Cl(OH)SO^3H$ (Darmstaedter, *Zeitschr. f. Chem.* [2] iv. 342):



Epichlorhydrin heated with a concentrated solution of 2 mol. *neutral potassium sulphite* in a retort with upright condenser, yields the dipotassic salt of disulphoglyceric acid, $C^3H^6S^2O^7K^2 + 2H^2O$, together with free potash, the reaction probably taking place in two stages, as follows:



and



(Patzschke, *Zeitschr. f. Chem.* [2] v. 612.)

Epichlorhydrin unites directly with *hypochlorous acid*, when added to a cooled solution of that acid containing from 6 to 8 p. c. ClOH, and protected from light, forming the dichlorhydrin $(C^3H^4)^{iv}(OH)^2Cl^2$, corresponding to the tetratomic alcohol, propylphycite, $(C^3H^4)^{iv}(OH)^4$ (v. 894):

$$C^3H^5OCl + HOCl = C^3H^6O^2Cl^2$$

(Carius, *Ann. Ch. Pharm.* cxxxiv. 71).

Epichlorhydrin unites directly with *acid chlorides* and *anhydrides*, forming chlorhydrins containing the corresponding acid radicles, the proportions in which the combination takes place varying according to the temperature and circumstances of the reaction. Thus with *acetyl chloride* at ordinary temperatures, after long standing, or more quickly at 100°, it forms *acetodichlorhydrin*, $C^3H^5\left\{\begin{matrix}OC^2H^3O\\Cl^2\end{matrix}\right. = C^3H^5OCl + C^2H^3OCl$. In like manner is formed *butyrodichlorhydrin*, $C^3H^5(OC^4H^7O)Cl^2$. With *benzoyl chloride* at 180° it forms benzodichlorhydrin, $C^3H^5(OC^7H^5O)Cl^2$.

Epichlorhydrin and acetic chloride heated for thirty hours to 100° in sealed tubes form (besides acetodichlorhydrin), *diglycerin-acetotrichlorhydrin*, $\begin{matrix}(C^3H^5)'''\\(C^3H^5)'''\end{matrix}\left\{\begin{matrix}OC^2H^3O\\O''\\Cl^3\end{matrix}\right.$ and *triglycerin-acetotetrachlorhydrin*, $\left.\begin{matrix}(C^3H^5)'''\\(C^3H^5)'''\\(C^3H^5)'''\end{matrix}\right\}\left\{\begin{matrix}OC^2H^3O\\O^2\\Cl^4\end{matrix}\right.$, produced respectively by the union of 2 or 3 mol. epichlorhydrin with 1 mol. acetyl chloride. Epichlorhydin heated for four hours to 180° with acetic anhydride yields *diacetochlorhydrin*, $(C^3H^5)'''\left\{\begin{matrix}(OC^2H^3O)^2\\Cl\end{matrix}\right. = C^3H^5OCl + (C^2H^3O)^2O$; and when heated with acetic anhydride for 20 hours to 200° it forms (besides the last-mentioned compound) a body having the composition $\left.\begin{matrix}(C^3H^5)'''\\(C^2H^3O)^4\end{matrix}\right\}\left\{\begin{matrix}O^2\\Cl\end{matrix}\right. = C^3H^5OCl + 2(C^2H^3O)^2O$ (Truchot, *Bull. Soc. Chim.* [2] v. 447; vi. 481).

CHLORINE. The following methods of preparation on the large scale have been proposed as capable, under particular circumstances, of advantageously replacing the ordinary method of decomposing hydrochloric acid with manganese dioxide:

1. Binks and Macqueen (*Technologiste*, 1862, p. 627) heat a mixture of 2 mol. magnesium chloride and 1 mol. manganese dioxide, whereby 2 mols. magnesia and 1 mol. manganous chloride are formed and 1 mol. chlorine is given off:

$$2MgCl^2 + MnO^2 = 2MgO + MnCl^2 + Cl^2.$$

A similar method is described by Clemm (*Journal of Gas-lighting*, 1863, p. 385).

2. Schlösing (*Rép. Chim. pure*, iv. 378) proposes to heat a mixture of hydrochloric and nitric acids, suitably concentrated, with manganese dioxide, whereby chlorine, manganous nitrate, and water are produced. The manganous nitrate heated to between 150° and 195° yields manganese dioxide and nitrogen tetroxide; the latter under the influence of water and oxygen reproduces nitric acid, which, together with the manganese dioxide, may be used for the decomposition of a fresh quantity of hydrochloric acid. In one experiment, using 4 equivalents of nitric acid containing 50·5 p. c. N^2O^5, and 3 eq. of hydrochloric acid containing 39·5 p. c. HCl, these acids being diluted with $\frac{1}{7}$ of their volume of water and heated to 122°, Schlösing obtained 91 p. c. of the chlorine contained in the hydrochloric acid, recovering at the same time 93·3 p. c. of the manganese and 91 p. c. of the nitric acid. This method seems therefore to promise well for application on the manufacturing scale.

3. Laurens (*Rép. Chim. app.* iv. 110) mixes cupric chloride, $CuCl^2$, with half its weight of sand, dries the mixture, and heats it to 250°–300° in an earthen retort. The residue, consisting of cuprous chloride, Cu^2Cl^2, is reconverted into cupric chloride by exposure to the air in contact with hydrochloric acid.

4. Mallet (*Bull. Soc. Chim.* [2] vii. 522) directs a current of air over cuprous chloride heated to 100°, whereby an oxychloride Cu^2Cl^2O is formed, which is decomposed by hydrochloric acid into cuprous chloride, water, and free chlorine:

$$Cu^2Cl^2O + 2HCl = Cu^2Cl^2 + H^2O + Cl^2.$$

In a subsequent paper (*Compt. rend.* lxvi. 349) Mallet states that between 100° and 200°, and even at higher temperatures, cuprous chloride is almost instantly converted into oxychloride in a stream of moist air, and that the latter, if hydrochloric acid be slowly dropped upon it at the same time, may be converted into cupric chloride, which gives off chlorine when further heated.

5. H. Deacon finds that when a mixture of hydrochloric and oxygen gas is passed over cupric sulphate or other copper salt heated to 700°–750° F., the hydrochloric acid is completely decomposed, its hydrogen combining with the oxygen, and the chlorine being set free. The best way of conducting the process is to pass the mixed gases over pieces of brick soaked in solution of cupric sulphate and dried. Lead-salts, except the sulphate, act in the same manner, but require a higher temperature; also manganese salts, but less completely. The action of all these salts appears to be catalytic (*Chem. News*, September 30, 1870). This process is now carried out on the manufacturing scale. For other processes, see Richardson a. Watts's *Chemical Technology*, pt. iii. p. 386.

In the ordinary method of preparing chlorine by oxidising hydrochloric acid with manganese dioxide, the waste still-liquors, consisting of solution of manganous chloride and ferric chloride, have always been an incumbrance to the manufacturer, and have hitherto been but little utilised. Methods of reconverting the manganese contained in these liquids into dioxide have however been proposed, and to a certain extent carried out. Dunlop and Balmain neutralise the liquid with crude ammonium carbonate (from ammoniacal gas-liquor), which throws down ferric oxide, and then precipitate the decanted solution completely with a fresh proportion of ammonium carbonate, which throws down manganous carbonate. The latter dried and calcined in a muffle is converted into a mixture of dioxide and an intermediate oxide. Calcium carbonate may also be used instead of ammonium carbonate.—P. W. Hofmann (*Dingl. pol. J.* clxxxi. 364) recommends the following process. The impure manganous solution neutralised with chalk or lime is precipitated with calcium sulphide (for which purpose the yellow liquid obtained by lixiviating soda-waste after exposure to the air may be used); and the precipitate of manganous sulphide and sulphur separated after 24 hours is dried at a gentle heat. It then contains about 57 p. c. sulphur, and forms a good material for burning in pyrites burners. Hofmann obtained from it 41 p. c. sulphur in the form of sulphurous oxide, and a residue consisting of 75·4 p. c. manganous sulphate, 8·8 p. c. manganese dioxide, and 15·8 p. c. manganous oxide. The latter gently heated with sodium nitrate (2 mol. $NaNO^3$ to 1 mol. MnO or $MnSO^4$) yields, with evolution of nitrous vapours, a mixture of sodium sulphate and the higher oxides of manganese. The washed and dried product yields on the average a quantity of available oxygen equivalent to 55 p. c. MnO^2. Any iron that may be present in the crude manganese solution may be separated before the precipitation, by addition of a small quantity of soda residue.

W. Weldon (*Laboratory*, i. 445) precipitates the crude manganese solution in the generating vessel with slaked lime, and passes a stream of air into the liquid in order to bring the manganese to a higher state of oxidation. The resulting solution of calcium chloride is decanted after subsidence. The oxide of manganese thus obtained is said to correspond to 55 p. c. dioxide. For a full description of this process, which is now largely employed, see *Chemical News*, Sept. 23, 1870.

Kuhlmann (*Compt. rend.* xlvii. 403) utilises the manganese residues for the preparation of barium chloride, by heating them, after evaporation to dryness, with a mixture of native barium sulphate and charcoal:

$$MnCl^2 + SO^4Ba + C^4 = BaCl^2 + MnS + 4CO.$$

The barium chloride is extracted by lixiviation.

Lastly, these liquors, which contain free chlorine, as well as manganous, manganic, and ferric chlorides, are utilised by E. Kopp at Dieuze for the recovery of sulphur from soda-waste. The sulphur which is contained in them as sulphide and hyposulphite of calcium, &c., is separated by the action of the manganese liquor, partly in the free state, partly as hydrogen sulphide: 10,000 litres of manganese liquor yield on the average 36 kilos. of pure sulphur. An additional quantity is recovered by burning the hydrogen sulphide with a limited supply of air (*Ann. Ch. Phys.* [4] vii. 5, 63; *Bull. Soc. Chim.* [2] iv. 335, 440; *Jahresb.* 1865, p. 779).

Physical Properties of Chlorine.—From the experiments of E. Ludwig (*Zeitschr. f. Chem.* [2] v. 172) it appears that chlorine does not conform to Gay-Lussac and Mariotte's laws till raised to temperatures considerably above its point of condensation. Its specific gravities at different temperatures were found to be as follows:

Temp.	Sp. gr.	Temp.	Sp. gr.
20°	2·4807	150°	2·4609
50	2·4783	200	2·4502
100	2·4685		

The density calculated from the atomic weight determined by Stas (35·457) is 2·45012.

Chlorine gas liquefies under a pressure of six atmospheres at 0°, and under eight and a half atmospheres at 12·5° (Niemann). Liquid chlorine boils under the ordinary atmospheric pressure at −33·6° (Regnault, *Jahresb.* 1863, p. 70). According to Loir a. Drion (*Bull. Soc. Chim.* 22 juin 1850), chlorine does not liquefy under ordinary pressure at −34°; but at the temperature of −50°, obtained by blowing air over liquid sulphurous oxide, the liquefaction takes place.

Chlorides.

Hydrogen Chloride. Hydrochloric Acid. Among various methods suggested for the preparation of this acid on the manufacturing scale, may be mentioned the decomposition of calcium chloride by aqueous vapour at a high temperature. The calcium chloride obtained by treating the still-liquors of the chlorine manufacture with calcium carbonate (p. 435) may be utilised for this purpose (Pelouze, *J. Chim. méd.* [4] vi. 197; *Compt. rend.* lii. 1267). At present, however, by far the greater part of the hydrochloric acid used in the arts is obtained as a secondary product in the decomposition of common salt by sulphuric acid for the production of sodium sulphate in the soda manufacture, the vapour of hydrochloric acid thereby evolved being condensed by passing through towers filled with fragments of coke or stone, down which a continuous stream of water is made to flow (v. 610). For details, see Richardson and Watts's *Chemical Technology*, vol. i. pt. iii. pp. 204–215, and pt. v. pp. 235–244.

Hydrochloric acid free from *arsenic* may be readily obtained by distilling the crude commercial acid with fuming solution of stannous chloride, filtering after twenty-four hours from the precipitated metallic arsenic (p. 217), and distilling from a retort, the receiver being changed after the first tenth has passed over (Bettendorff, *Zeitschr. f. Chem.* [2] v. 493). P. W. Hofmann (*ibid.* 253) prepares pure hydrochloric acid by filling a bottle having a twice perforated stopper, to one-third of its volume, with the crude acid, and adding sulphuric acid of sp. gr. 1·848 through a stoppered funnel. Hydrochloric acid gas is then immediately evolved, and may be collected, after washing, in distilled water.

Gaseous hydrogen chloride is somewhat quickly decomposed by a glowing spiral of iron wire, or by the electric arc between iron points, white fumes of ferrous chloride being formed and the volume of the gas reduced to one-half; the decomposition is, however, not quite complete, even after the experiment has been continued for several hours. The induction-spark produces a scarcely perceptible diminution of volume even when continued for a long time (Buff a. Hofmann, *Chem. Soc. Qu. J.* xii. 273).

When air mixed with vapour of hydrochloric acid is passed into a warm solution of potassium permanganate mixed with sulphuric acid, or through a mixture of manganese dioxide and sulphuric acid, the hydrochloric acid is oxidised to hypochlorous acid, HClO (Odling, *Pharm. J. Trans.* [2] i. 469).

Hydrochloric acid gas is absorbed by solid *nitrogen tetroxide* (iv. 76), forming a liquid which by repeated fractional distillation, may be separated into two liquid compounds, one boiling at −5°, the other at +5. The former is Gay-Lussac's chloronitric acid, $NOCl^2$ (iv. 116); the latter has the composition NO^2Cl (R. Müller, *Ann. Ch. Pharm.* cxxii. 1).

Aqueous hydrochloric acid heated to 200° for sixteen hours with amorphous *phosphorus* gives off gas and yields a solution of phosphorous acid; apparently thus: $3HCl + P^2 = PH^3 + PCl^3$; and $PCl^3 + 3H^2O = 3HCl + PH^3O^3$ (Oppenheim, *Bull. Soc. Chim.* [2] i. 163).

Anhydrous liquid hydrochloric acid is much less energetic in its chemical reactions than the aqueous acid: it does not attack magnesium, zinc, iron, lime, metallic sulphides, or certain carbonates. Potassium, sodium, tin, and lead are attacked, but without evolution of gas; aluminium dissolves in it quickly, with effervescence (Gore, *Phil. Mag.* [4] xxix. 541).

Metallic chlorides are decomposed by aqueous vapour at high temperatures, yielding metallic oxides and hydrochloric acid. With the chlorides of the heavy metals, especially those which are volatile, this decomposition takes place easily, also with the chlorides of aluminium and magnesium. The chlorides of calcium and strontium are decomposed more slowly, whereas those of barium, potassium, and sodium are not decomposed by aqueous vapour alone, but only in presence of silica; lithium chloride, on the other hand, is decomposed by aqueous vapour alone (Kuhnheim, *Jahresb.* 1861, p. 149).

The reactions of metallic chlorides with *ammonia* are described in the Dictionary under the chlorides of the respective metals: see also Deherain (*Compt. rend.* lii. 734; *Rép. Chim. pure*, 1861, p. 215). On the action of *nitric acid* on metallic chlorides, see H. Wurtz (*Sill. Am. J.* [2] xxv. 371; *Jahresb.* 1858, p. 604); of phosphorus pentachloride (iv. 512).

TRANSFORMATION OF CHLORINATED INTO IODATED ORGANIC COMPOUNDS.

Ad. Lieben has made important experiments on this kind of transformation. Ethyl chloride, mixed in a sealed tube with three or four times its weight of strong hydriodic acid, sp. gr. 1·9, and heated for five hours to 130°, is almost wholly converted into ethyl iodide, according to the equation:

$$C^2H^5Cl + HI = C^2H^5I + HCl.$$

In like manner ethylated ethyl chloride (butyl chloride) and amyl chloride are converted by strong hydriodic acid into the corresponding iodides, without formation of secondary products. Ethylchlorinated ethyl oxide $\left.\begin{matrix}C^2H^4(C^2H^5)Cl\\ C^2H^5\end{matrix}\right\}O$ is converted, by an excess of strong hydriodic acid, chiefly into ethyl iodide and ethylated ethyl iodide (butyl iodide); but there are also some secondary products formed, viz. butyl chloride, alcohol, and a substance having a carbonaceous aspect, the quantity of these secondary products increasing as the hydriodic acid is less concentrated and present in smaller quantity. To determine whether the action of hydriodic acid is a simple double decomposition or a case of the action of masses, the converse reaction was tried by heating ethyl iodide with a considerable excess of hydrochloric acid in a sealed tube to 130°. A small quantity of ethyl-chloride was thereby obtained, together with hydriodic acid and free iodine, showing that the inverse of the first-described reaction does really take place; but the quantity of ethyl chloride which it yields is very small, even when the action is continued for fifty hours. The result of the two supplementary experiments, namely, the decomposition of ethyl chloride by hydrogen iodide, and of ethyl iodide by hydrogen chloride, may be represented, though somewhat crudely, in the following manner:

$$\begin{aligned}&(\text{Affinity of H for I}) + (\text{Affinity of } C^2H^5 \text{ for Cl})\\ < \ &(\text{Affinity of H for Cl}) + (\text{Affinity of } C^2H^5 \text{ for I}).\end{aligned}$$

The decomposition of ethyl chloride and its homologues by the action of hydriodic acid, is analogous to the decomposition of silver iodide by the same reagent. As an example of the action of hydriodic acid on organic chlorides of other series, *chloroform* $CHCl^3$ was introduced, together with eleven times its weight of hydriodic acid of sp. gr. 1·9, into a sealed tube, and heated for seven hours to 125°. The principal results of this reaction were hydrochloric acid, free iodine, and methylene iodide, CH^2I^2. Now, remembering the fact, demonstrated by Kekulé, that iodides submitted to the action of hydriodic acid undergo an inverse substitution, the reaction just described may be explained by supposing that the chloroform is in the first instance converted into iodoform, which is then converted into methylene iodide by the action of the hydriodic acid, thus:

$$CHCl^3 + 3HI = CHI^3 + 3HCl$$

and

$$CHI^3 + HI = CH^2I^2 + I^2.$$

In other cases, the action represented by the second equation goes so far as to remove all the iodine from the iodated product formed in the first instance, and convert it into the corresponding hydride. Such, indeed, is the case with compounds belonging to the aromatic series. Berthelot (*Bull. Soc. Chim.* [2] ix. 30) has shown that Julin's chloride of carbon, or perchlorinated benzene, C^6Cl^6, is converted into benzene, C^6H^6, when heated to 280° with a large excess of hydriodic acid; and Lieben finds that monochlorobenzene, C^6H^5Cl, heated to 235°, for fifteen hours, with from three to five times its weight of hydriodic acid, likewise yields benzene.

The action of hydriodic acid on organic chlorine-compounds appears, then, to exhibit two cases: 1. The chloride is easily converted into the corresponding iodide by double decomposition, whereas the transformation of the iodide into the corresponding hydride is difficult, and takes place only at high temperatures. In this case, if the experiment is well conducted, an iodide is obtained without a trace of hydride. Such is the case in the action of hydriodic acid on the chlorides of the series $C^nH^{2n+1}Cl$.—2. The chloride is attacked by hydriodic acid with difficulty, and only at a high temperature, whereas the conversion of the iodide into hydride takes place easily, and at a comparatively low temperature. In such cases, as with the chlorides of the aromatic series, the product of the reaction is a hydride without any trace of iodide. In some cases, as that of chloroform, intermediate products are obtained, only part of the iodine being removed by the inverse reaction (*Giornale di Scienze di Palermo*, v. 130).

CHLORINE, OXYGEN-ACIDS OF. These acids, with the exception of perchloric acid, are reduced by nitrous acid; chloric acid in the first instance to chlorous acid; chlorous and hypochlorous acids immediately to hydrochloric acid:

$$HClO^3 + HNO^2 = HNO^3 + HClO^2$$
$$HClO^2 + 2HNO^2 = 2HNO^3 + HCl$$
$$HClO + HNO^2 = HNO^3 + HCl.$$

Perchloric acid is not altered by heating with nitrous acid, even in concentrated solution (Toussaint, *Ann. Ch. Pharm.* cxxxvii. 114).

Hypochlorous Oxide, Acid, and Salts. Hypochlorous oxide gas is absorbed by *sulphuric oxide*, forming a dark red thickish liquid, which on cooling solidifies to a mass of slender needles consisting of $Cl^2O.4SO^3$. This compound melts at about 55°, is instantly resolved by water into hypochlorous and sulphuric acids, acts upon iodine, with evolution of chlorine and formation of iodic acid, and as a powerful oxidising agent on sugar, alcohol, and other organic bodies. When quickly heated, it detonates. Hypochlorous oxide is likewise absorbed by liquid *sulphurous oxide*; but as soon as the containing vessel is removed from the freezing mixture, a rapid evolution of chlorine takes place, and a red viscid liquid is left, containing hypochlorous and sulphuric oxides in a proportion not yet determined (Schützenberger, *Compt. rend.* lii. 135).

Carius (*Ann. Ch. Pharm.* cxxvi. 129) prepares a 2 to 3 p. c. solution of hypochlorous acid containing mercuric oxychloride and excess of mercuric oxide, by agitating mercuric oxide, previously heated to 300° and suspended in a small quantity of water, with chlorine gas as free as possible from air (15 grms. HgO to 1 litre of chlorine) in a dark place, in bottles provided with glass stoppers and not holding more than a litre; with larger quantities, the preparation fails in consequence of the formation of mercuric chlorate. The aqueous acid thus obtained is mixed with a small quantity of precipitated mercuric oxide previously heated to 300°. Such a solution is better adapted for certain experiments on organic bodies than pure hypochlorous acid, which easily gives off chlorine even in very dilute solution.

Hypochlorous acid unites directly with many unsaturated organic compounds, *e.g.*, with *ethylene*, forming ethylene oxychloride or glycolic chlorhydrin, $C^2H^4\left\{\begin{matrix}OH\\Cl\end{matrix}\right.$; with *amylene* in like manner, forming $C^5H^{10}\left\{\begin{matrix}OH\\Cl\end{matrix}\right.$; with *glyceric epichlorhydrin*, C^3H^5OCl, forming the dichlorhydrin of propyl-phycite, $(C^3H^4)^{iv}\left\{\begin{matrix}(OH)^2\\Cl^2\end{matrix}\right.$, &c. (Carius). With *turpentine oil*, it also forms a dichlorhydrin, $C^{10}H^{16}\left\{\begin{matrix}(OH)^2\\Cl^2\end{matrix}\right.$, which dissolves in the aqueous liquid and may be extracted therefrom by ether; and likewise a viscid liquid apparently containing di- and tri-chlorinated turpentine oil. With *camphor* it forms monochlorocamphor, $C^{10}H^{15}ClO$ (Wheeler, *Zeitschr. f. Chem.* [2] iv. 170).

Calcium Hypochlorite.—The constitution of bleaching powder has lately been examined by J. Kolb (*Ann. Ch. Phys.* [4] xii. 266; *Jahresb.* 1867, p. 192), who finds that the most concentrated preparation producible by saturating dry calcium hydrate with chlorine contains 38·5 p. c. bleaching chlorine, 45·8 lime, and 24·7 water, corresponding with the formula $3CaH^2O^2 + 4Cl$ or $CaH^2O^2 + 2(CaO.H^2O.Cl^2)$ or $Ca^3H^6O^6.Cl^4$. In this product, the water and the whole of the lime are essential constituents, which cannot be removed without complete decomposition of the compound. Commercial bleaching powder always contains a slight excess of water, as well as free lime, which gives it greater stability, an effect likewise produced by other inactive substances, such as carbonate and sulphate of calcium. Dry chloride of lime is decomposed by water, with separation of calcium-hydrate and formation of a solution containing chloride and hypochlorite of calcium:

$$Ca^3H^6O^6Cl^4 = \underset{\text{Hydrate.}}{CaH^2O^2} + \underset{\text{Chloride.}}{CaCl^2} + \underset{\substack{\text{Hypo-}\\\text{chlorite.}}}{Ca(ClO)^2} + 2H^2O.$$

This agrees with the result formerly obtained by Fresenius (iii. 237). Hence it appears that the solution of bleaching powder differs materially in constitution from the dry product, which does not appear to contain a ready-formed hypochlorite; in fact the dry compound and the solution differ materially in their modes of decomposition under the influence of free chlorine and of heat. (*a*) Dry bleaching powder is not altered at ordinary temperatures by an excess of chlorine; but the solution when thus treated becomes strongly acid; and on afterwards expelling the excess of chlorine from the solution by a current of carbon dioxide, the quantity of bleaching chlorine (that is in the form of hypochlorous acid) in the liquid is found to have doubled; thus:

$$CaCl^2 + Ca(ClO)^2 + Cl^4 + 2H^2O = 2CaCl^2 + 4HClO.$$

This reaction may serve for the preparation of hypochlorous acid.

(*b*) Under the influence of heat (at 80°–90° if it is poor, at 40°–35° if it is rich) dry chloride of lime is converted into chlorate, becoming pasty in consequence of the separation of water:

$$3Ca^3H^6O^6Cl^4 = 5CaCl^2 + Ca(ClO^3)^2 + 3CaH^2O^2 + 6H^2O.$$

The dissolved chloride is much less alterable, and it is only at the boiling heat and when concentrated that it is converted into chlorate, with evolution of oxygen and chlorine. In direct sunshine, the dry chloride is decomposed in the same manner as when heated, though less quickly; the dissolved chloride is partly converted into chlorite.

Dry chloride of lime is completely decomposed by dry carbon dioxide, with evolution of chlorine, whereas from the aqueous solution, even the greatest excess of carbon dioxide precipitates only half the calcium as carbonate, and with separation of hypochlorous acid, which does not act upon the residual calcium chloride. The same behaviour is exhibited by solid chloride of lime in moist air, whence it appears that in the use of bleaching powder for disinfecting the air, the active agent is not free chlorine, but hypochlorous acid.

According to Scheurer-Kestner (*Bull. Soc. Chim.* [2] ix. 159), a slight elevation of temperature (to about 55°) consequent on the absorption of the chlorine is not disadvantageous in the production of bleaching powder; but an excess of chlorine actually diminishes the proportion of that element in the product available for bleaching, apparently in consequence of the formation of chlorite. When a rather thick layer of slaked lime is saturated with chlorine, the superficial portion is always inferior in bleaching power to the lower portions.

Solutions of bleaching powder or of pure calcium hypochlorite exposed to sunlight give off ordinary oxygen, yielding at the same time chlorite as well as chlorate of calcium.

For the analysis of bleaching powder Kolb (*loc. cit.*) estimates the bleaching chlorine volumetrically by Gay-Lussac's method with arsenious acid (i. 904), and the entire amount of chlorine present as chloride and hypochlorite, in another portion, by precipitation with silver nitrate, after previous warming with ammonia to convert the hypochlorite into chloride:

$$3Ca(ClO)^2 + 4NH^3 = 3CaCl^2 + 6H^2O + N^4.$$

In perfectly normal chloride of lime, $Ca^3H^6O^6Cl^4$, the two processes give the same result; but if part of the chlorine is in the form of chlorate, the second method will give an excess of chlorine. To determine the amount of chlorate present, a third portion is heated with ammonia, then strongly acidulated with sulphuric acid, metallic zinc is introduced, and the mixture is left for some hours, to convert the chlorate into chloride by the action of the nascent hydrogen. If after this treatment the amount of chlorine determined by precipitation with silver nitrate is greater than that given by the second method, the difference is to be estimated as chlorate.

Magnesium Hypochlorite.—According to Bolley a. Jokisch (*Bull. Soc. Chim.* [2] vii. 524), a solution of chloride of magnesia, obtained by precipitating a solution of chloride of lime with magnesium sulphate, or by passing chlorine into water in which magnesia is suspended, exerts a quicker and at the same time a milder bleaching action than the solution of chloride of lime. Bolley attributes this difference, partly to the more ready decomposibility of magnesium hypochlorite, partly to the fact that magnesia does not possess caustic properties.

Silver Hypochlorite. $ClOAg$.—When chlorine in excess is passed into water in which oxide or carbonate of silver is suspended, the silver is converted into chloride, and an aqueous solution of hypochlorous acid is formed without a trace of chlorate or chlorite. But if the silver oxide is in excess, and the liquid is repeatedly shaken during and after the passage of the chlorine, silver chloride and hypochlorous acid are formed indeed in the first instance as before, but the latter gradually reacts with the excess of silver oxide, forming silver hypochlorite, so that ultimately the liquid loses the smell of hypochlorous acid. The very soluble silver hypochlorite remains undecomposed, and the solution retains its transparency as long as the agitation with excess of silver oxide is kept up; but when left at rest, the hypochlorite is quickly resolved into chloride and chlorate. These reactions may be represented by the following equations:

$$\begin{aligned} 3Ag^2O + 12Cl + 3H^2O &= 6AgCl + 6HClO \\ 6HClO + 3Ag^2O &= 6AgClO + 3H^2O \\ 6AgClO &= 4AgCl + 2AgClO^3. \end{aligned}$$

Chlorous Oxide, Cl^2O^3, and **Acid,** $HClO^2$.—Schiel (*Ann. Ch. Pharm.* cix. 317) prepares chlorous oxide by means of a mixture of 3 pts. nitric acid of sp. gr. 1·3, 2 pts. potassium chlorate, 0·6 to 0·8 pt. cane-sugar (instead of the tartaric acid recommended by Millon), and 3 to 4 pts. water: it is not necessary to pulverise the chlorate or the sugar. The mixture is poured into a flask standing in a water-bath, in such quantity that the neck of the vessel above the bath may be half filled with the liquid when expanded by the heat. The mixture may be heated to 60° or even to 100° without danger of explosion, provided that the gas evolved from two separate flasks is not directed into the same absorption-vessel.

Brandau (*Ann. Ch. Pharm.* cli. 340) prepares chlorous oxide by reduction of chloric acid with sulphobenzolic acid, a method first practised by Carius (*Zeitschr. f. Chem.* [2] iv. 17). 10 pts. of pure benzene are dissolved in 100 pts. of hydrogen sulphate diluted with 100 pts. water, and when the mixture has cooled 12 pts. of pulverised potassium chlorate are added. The mixture is heated to 50° in a flask having a delivery tube fitted to its neck by grinding, and blown out here and there into small bulbs; and the gas, after passing through water contained in these bulbs, is conducted into a glass tube standing in a mixture of ice and salt. The condensed liquid deposits crystals of a hydrate of chlorous acid, and the supernatant liquid decanted immediately into a small cooled glass cylinder, forms nearly anhydrous chlorous oxide. The gaseous chlorous oxide prepared by the older methods is too much contaminated with free chlorine to admit of condensation by a mixture of ice and salt (i. 909).

Liquid chlorous oxide thus obtained is very mobile, has a deep red-brown colour, and when recently condensed, a sp. gr. of 1·330 to 1·387 at 0°, referred to water at 4°. A drop of the recently condensed liquid evaporates on a watchglass without residue even at temperatures below 0°. It boils a little above 0°, but the boiling point of the last portions rises to 8°; the liquid also acquires a higher boiling point by keeping. A drop of this less volatile liquid leaves on evaporation a residue of chloric acid. Hence it appears probable that the condensed chlorous oxide contains a certain quantity of the compound Cl^2O^4 or chloroso-chloric anhydride $\left.\begin{matrix}ClO\\ClO^2\end{matrix}\right\}O$. Liquid chlorous oxide explodes somewhat readily at a few degrees above 0°. The sp. gr. of gaseous chlorous oxide prepared from the recently condensed liquid was found to be 4·022 at 13°, and 4·070 at 9°, the formula Cl^2O^3 requiring 4·123 (Brandau).

When the gas is passed into water at 0°, the chlorous oxide separates in resinous drops or granules, which if agitated with the water after the passage of the gas has ceased, are converted into a yellow lamino-crystalline *hydrate* of somewhat variable constitution: it may be heated to 10° without fusion, but volatilises slowly without residue even considerably below that temperature (Brandau).

According to Schiel, water dissolves about 10 times its weight of chlorous oxide, forming a deep golden-yellow liquid, which may be kept for some time without alteration, and possesses fourteen times the bleaching power of chlorine-water. According to Brandau, 100 grms. of water dissolve:

At 8·5° and 752·9 mm. pressure, 4·7655 grm. chlorous oxide.
„ 14° „ 756·3 „ 5·0117 „ „
„ 21° „ 754 „ 5·4447 „ „
„ 23° „ 760 „ 5·6508 „ „

When the aqueous solution is heated to 50°, chloric and hydrochloric acids are abundantly formed, the latter acting further on the chlorous acid, with evolution of chlorine: hence it is not possible to obtain pure chloric oxide gas by heating the aqueous solution or by decomposing the solution of a chlorite. On mixing aqueous chlorous acid with potassium iodide and hydrochloric acid, iodine is separated according to the equation:

$$Cl^2O^3 + 8HI = 2HCl + 3H^2O + 4I^2.$$

Most metals are without action on gaseous chlorous oxide; but *mercury* absorbs it at ordinary temperatures. Most of the non-metallic elements decompose it with detonation. It is decomposed very quickly by direct sunshine, more slowly by diffused daylight; the presence of a trace of moisture facilitates the decomposition (Schiel).

Gaseous chlorous oxide is absorbed by dry *glycerin*. After a certain time an explosion takes place, which, however, is not strong enough to break the vessel; afterwards the absorption becomes rapid, but not tumultuous. With *ethylic* and *amylic alcohols*, chlorous oxide produces ethylic acetate and amylic valerate; thus:

$$4C^2H^6O + Cl^2O^3 = 2(C^2H^3O^2.C^2H^5) + 3H^2O + 2HCl.$$

Urea dissolves in aqueous chlorous acid, evolving carbon dioxide, and probably nitrogen monoxide. If the proportion of chlorous acid present is such that the liquid remains sensibly greenish after warming, the solution evaporated at 100° leaves a crystalline compound containing CH^3N^2ClO. The reaction is probably as follows:

$$4CH^4N^2O + Cl^2O^3 = 2CH^3N^2ClO + 2CO^2 + N^2O.$$

With *uric acid*, chlorous acid forms chloraluric acid (i. 885), together with other products (Schiel, *Ann. Ch. Pharm.* cxii. 73).

Chlorates. For the quantitative estimation of chloric and of chlorous acid, Toussaint recommends a method founded on the reaction of these acids with nitrous acid already described (p. 438). The aqueous solution of the salt to be examined is mixed with a slight excess of lead nitrite acidulated with nitric acid, and the chlorine is then precipitated as silver chloride. Or it may be mixed with a titrated solution of lead nitrite, and the completion of the reaction indicated by addition of a quantity of silver nitrate more than sufficient for the complete precipitation of the chlorine. The solution of lead nitrite is prepared by treating the basic nitrite $Pb(NO^2)^2.3PbO.H^2O$ suspended in water with carbonic acid, till it disappears completely and a yellow solution of the nitrite is formed which is no longer rendered turbid by carbonic acid. For the volumetric estimation, this solution is titrated with a normal solution of potassium chlorate, and diluted so that 1,000 c.c. of it shall correspond to 6·14 grms. potassium chlorate (*Ann. Ch. Pharm.* cxxxvii. 114; *Jahresb.* 1866, p. 787).

Stelling (*Zeitschr. anal. Chem.* vi. 32) estimates the chlorine in chlorates by heating the solution to boiling with ferrous sulphate and potash, and precipitating the chlorine from the filtered solution (after oxidation with nitric acid) with silver nitrate:

$$KClO^3 + 6FeO = KCl + 3Fe^2O^3.$$

The same method serves for estimating the total amount of chlorine in hypochlorites.

Barium Chlorate, $(ClO^3)^2Ba$, is easily prepared as follows: Potassium chlorate is heated on the water-bath with commercial aluminium sulphate and sulphuric acid in rather more than equivalent quantities, whereby crystallised alum and chlorous acid are produced, the former separating on cooling:

$$(SO^4)^3Al^2 + SO^4H^2 + 2ClO^3K = (SO^4)^4Al^2K^2 + 2ClO^3H.$$

The perfectly cooled mass is mixed with several times its volume of alcohol, filtered and washed with alcohol of 50 p. c; the alcoholic liquid is neutralised with barium hydrate; the greater part of the alcohol removed by evaporation; and the liquid filtered. The residue contains barium sulphate and aluminium hydrate; the solution, pure barium chlorate (Brandau, *Ann. Ch. Pharm.* cli. 361).

Basic Cupric Chlorate is thrown down on adding cupric acid to a boiling solution of potassium chlorate, as a green precipitate which decomposes quickly in washing.

Potassium Chlorate. ClO^3K.—The solubility of this salt in alcohol of various strengths has been determined by Gerardin (*Ann. Ch. Phys.* [4] v. 129). The following table gives the weights w of the salt, dissolved at the temperatures t in 100 pts. by weight of spirit of the specific gravities on the first line:

Alcohol of sp. gr.	0·9904		0·9793		0·9573		0·9390		0·8967		0·8429	
	t	w	t	w	t	w	t	w	t	w	t	w
Potassium Chlorate	13°	4·9	14°	3·2	13°	1·9	14·5°	1·1	12°	0·46	25°	0·09
	25	7·5	26	5·4	20	2·7	28	2·2	31	1·28	34	0·12
	35	10·2	38	7·9	36	4·3	40	3·4	43	1·95	56	0·24
	44	13·6	51	12·2	55	7·9	50	4·3	58	3·10	64	0·32
	50	16·2	63	17·5	63	10·5	67	7·6				

Potassium chlorate affords a very delicate test for the presence of manganese in organic bodies. When any substance containing manganese is thrown into melting potassium chlorate, the saline mass on cooling exhibits a rose-red or peach-blossom colour. The commercial salt itself, however, is seldom quite free from traces of manganese. To test it, a small quantity is to be fused, and a piece of charcoal prepared from pure sugar thrown into it; if manganese is present, a reddish colour will be apparent on cooling (Böttger, *J. pr. Chem.* lxx. 433). On the catalytic decomposition of potassium chlorate by manganese dioxide, cupric oxide, &c., see Wiederhold (*Pogg. Ann.* cxvi. 171; *Jahresb.* 1862, p. 76); also Krebs (*Zeitschr. f. Chem.* [2] vi. 243).

Rubidium Chlorate (v. 131).

Silver Chlorate. ClO^3Ag.—To obtain this salt perfectly pure, Stas (*Jahresb.* 1867, p. 312) passes a slow stream of chlorine into water containing oxide or carbonate of silver in suspension; decants the liquid (in which the alkali always present in precipitated silver oxide has been converted into hypochlorite) after a while, repeating this operation till the evaporated residue no longer contains any perceptible quantity of alkali; washes the silver precipitate carefully; suspends it in water; again treats it during agitation with chlorine gas, till the greater part of the silver oxide has taken part in the reaction; then agitates the mixture till its odour is quite destroyed. The clear liquid is decanted, left at rest (best at 60°) till the hypochlorite of silver is converted into chlorate, and the solution of silver chlorate is evaporated over the water-bath. The salt then remains as a white powder, which does not alter either in dry or in moist air. Any hygroscopic tendency indicates the presence of perchlorate.

Strontium Chlorate.—The solution evaporated over sulphuric acid leaves the salt in small granular crystals containing $(ClO^3)^2Sr.5H^2O$ (Souchay, *Ann. Ch. Pharm.* cii. 381).

Thallium Chlorate (v. 754).

Yttrium Chlorate, $(ClO^3)^2Y$, is obtained in crystalline laminæ by decomposing barium chlorate with yttrium sulphate, separating the excess of barium with dilute sulphuric acid, and evaporating (Popp, *Jahresb.* 1864, p. 204).

CHLOROFORM. $CHCl^3$. *Trichloromethane. Dichlorinated Methyl chloride.*—This compound boils at 60·16° (Regnault, *Jahresb.* 1863, p. 70). It is formed by the action of zinc and sulphuric or hydrochloric acid on carbon tetrachloride in a flask provided with an upright condensing tube, and is converted by the prolonged action of the same reducing agent into methylene chloride, CH^2Cl^2 (Geuther, *Ann. Ch. Pharm.* cvii. 212). It is also converted into methylene chloride and marsh gas by treating it in like manner with zinc and a little aqueous ammonia (Perkin, *Chem. News,* xviii. 106). Heated to 125° in sealed tubes for 7 hours with 11 pts. of strong hydriodic acid (sp. gr. 1·9), it yields methylene iodide, CH^2I^2, together with hydrochloric acid and free iodine: probably iodoform is produced in the first instance, and then converted into methylene iodide; thus:

$$CHCl^3 + 3HI = 3HCl + CHI^3$$

and

$$CHI^3 + HI = I^2 + CH^2I^2$$

(Lieben, *Zeitschr. f. Chem.* [2] iv. 713). Chloroform-vapour passed over red-hot *copper* is partially converted into acetylene (Berthelot, *Compt. rend.* l. 805). The same compound is formed by the action of *potassium amalgam* on liquid chloroform (Kletzinsky, *Zeitschr. f. Chem.* [2] ii. 127). Heated with *alcohol* and *potash* in sealed tubes to 100° for a week, it yields a certain quantity of ethylene gas (Berthelot, *Compt. rend.* xlvii. 350). Heated with an alcoholic solution of *sodium ethylate*, it yields an ether, $CH(OC^2H^5)^3$, which may be regarded as chloroform having its chlorine replaced by an equivalent quantity of oxethyl, or as the triethylic ether of a triatomic alcohol, $\left.\begin{matrix}(CH)'''\\H^3\end{matrix}\right\}O$, homologous with glycerin:

$$CHCl^3 + 3NaOC^2H^5 = 3NaCl + CH(OC^2H^5)^3$$

(Williamson a. Kay, *Chem. Soc. Qu. J.* vii. 224). According to Savitsch (*Bull. Soc. Chim.* avril 1860), this ether is more easily produced by the action of sodium on a cooled mixture of chloroform with excess of alcohol. According to Geuther (*Jahresb.* 1862, p. 388), chloroform heated with alcoholic potash gives off carbon monoxide. According to C. Schacht (*Jahresb.* 1867, p. 539), pure chloroform is decomposed by exposure to light and air; but in the dark it remains unaltered in a vessel only half filled with it.

Chloroform is slowly attacked by *alkaline sulphites* at 160°–180°. On opening the sealed tube, carbon dioxide escapes, together with a gas which burns with a green-edged flame (methyl chloride?) The solution contains methyl-sulphuric acid and its chlorinated derivatives, together with methylene-disulphuric and methenyl-trisulphuric acids. The simplest reaction is that which gives rise to dichloromethylsulphuric acid:

$$CHCl^3 + K^2SO^3 = CHCl^2SO^3K + KCl$$

In the formation of the other products, either an inverse substitution takes place, or the higher sulpho-acids at first produced are further decomposed, with separation of SO^2 (Strecker, *Zeitschr. f. Chem.* [2] iv. 214). Chloroform heated with an *alkaline cupric solution* throws down cuprous oxide:

$$CHCl^3 + 5KHO + 2CuO = Cu^2O + 3KCl + CO^3K^2 + 3H^2O.$$

The reaction is very delicate, one or two drops of chloroform shaken up with 100 c.c. of water immediately producing the red copper precipitate when warmed with the cupric solution. The same reaction is produced by all compounds which yield chloroform when treated with alkalis, such as chloral, trichloracetic acid, the perchloric ethers, &c. (Baudrimont, *J. Pharm.* [4] ix. 410).

CHLOROGENINE. $C^{21}H^{20}O^4$.—A base obtained by O. Hesse (*Ann. Ch. Pharm. Suppl.* iv. 40; *Jahresb.* 1865, p. 458) from the bark of an Australian tree not named. The concentrated very bitter aqueous extract of the bark, acidulated with sulphuric acid and mixed with mercuric chloride, yields a precipitate consisting of the mercurochloride of chlorogenine, while another base called *porphyrine* remains in solution. Chlorogenine separated from the mercury-compound, and precipitated by ammonia from the solution of its sulphate, is a coffee-coloured amorphous powder, easily soluble in acids when recently precipitated, soluble also in ammonia, fusel-oil, and especially in chloroform, with which it yields a solution red-brown by transmitted, green by reflected light. It is very bitter, and when swallowed produces uneasiness and tendency to vomit. It is the active and colouring principle of the bark, which contains 2½ p. c. of it. Its salts are amorphous.

CHLOROLITHINE. An altered felspar occurring in the old green porphyry of the Val Camonica. It is yellowish-green, of sp. gr. 2·92, and contains 47·3 p. c. SiO^2, 22·2 Al^2O^3, 9·8 Fe^2O^3, 8·6 CaO, 0·7 MgO, 3·3 K^2O, 4·6 Na^2O, and 2·7 H^2O (Tschermak, *Jahresb.* 1864, p. 869).

CHLOROPHYLL or *Leaf-green.* The nature of the green colouring matter of leaves is still but imperfectly known. According to Frémy (*Compt. rend.* l. 405; *Jahresb.* 1860, p. 533), it is composed of a blue substance, phyllocyanin, and a yellow substance, phylloxanthin, which may be separated by agitation with a mixture of ether and hydrochloric acid, the yellow substance dissolving in the ether, and the blue in the hydrochloric acid. Phyllocyanin is decolorised by alkalis, but regains its blue colour when treated with acids: hence also chlorophyll itself is turned yellow by alkalis and green again by acids. The blue and yellow constituents of chlorophyll may also be separated by boiling with baryta-water. On boiling the resulting precipitate with alcohol, uncombined phylloxanthin is dissolved, and there remains a baryta-lake from which the phyllocyanin may be separated by sulphuric acid and dissolved out by alcohol or ether. *Phylloxanthin* is a neutral substance insoluble in water, soluble in alcohol and ether, and crystallising therefrom in yellow laminæ or red prisms resembling those of potassium dichromate. It possesses very great colouring power, and dissolves with blue colour in strong sulphuric acid, whereas the yellow colour of flowers is coloured red by that acid. *Phyllocyanin* is insoluble in water, dissolves with olive-green or bronze-red colour in alcohol and ether; its salts are brown and green; those of the alkali-metals are soluble in water. The solutions of phyllocyanin in sulphuric or hydrochloric acid are green, reddish-violet, or blue, according to the degree of concentration: the phyllocyanin is precipitated from them by water (Frémy, *Ann. Ch. Phys.* [4] vii. 78; *Jahresb.* 1865, p. 586). H. Ludwig also finds that chlorophyll may be separated into a blue and a yellow colouring matter (iv. 634). Stokes, on the other hand (*Proc. Roy. Soc.* xiii. 144), concludes, from the optical properties of the chlorophyll of land-plants, that it is a mixture of four different colouring matters, two green and two yellow. The solutions of the green (but not of the yellow) colouring matters exhibit strong red fluorescence; three of these substances are very easily decomposed by acids or salts, acid potassium oxalate for example. Frémy's phyllocyanin is, according to Stokes, merely a product of decomposition of the green bodies by acids; it dissolves in many acids with green or blue colour, and in neutral solutions exhibits very sharp absorption-bands. Phylloxanthin varies in its properties according to the manner of its preparation. When prepared by removing the green substances by means of aluminium hydrate and a little water (iv. 634), it is a yellow substance; but when obtained with hydrochloric acid and ether, it is a mixture of the same yellow body with the products of decomposition of one of the green substances by acids. Green marine plants (*Chlorospermeæ*) differ from land-plants only in the relative proportions of the colouring matters above mentioned; olive-coloured sea-plants (*Melanospermeæ*), on the other hand, contain (instead of one of the green and one of the yellow bodies above-mentioned) another green and another yellow body. Red sea-plants (*Rhodospermeæ*) contain a red colouring matter in addition to the chlorophyll. Stokes further states that chlorophyll is easily distinguished from the green colouring matter of bile (biliverdin) by the fact that it exhibits very strong red fluorescence and very characteristic absorption-bands which are not exhibited by biliverdin.

According to Filhol (*Compt. rend.* lxi. 371; *Jahresb.* 1865, p. 586), chlorophyll dissolved in alcohol and cautiously treated is resolved into four substances: a brown azotised body insoluble in alcohol; a yellow non-azotised body soluble in alcohol; a blue substance formed only under the influence of an excess of hydrochloric acid; and a yellow body separated from the blue substance by ether. In a later investigation (*Compt. rend.* lvi. 1218; *Zeitschr. f. Chem.* [2] iv. 569) Filhol arrives at the following conclusions: 1. All methods of preparing chlorophyll by means of acids yield nothing but products of decomposition.—2. Organic acids, which act less strongly than mineral acids, destroy the green colour of chlorophyll solutions, and split up the chlorophyll into two substances, one of which separates in black flocks, while the other remains dissolved with fine yellow colour.—3. This yellow substance is further resolved by strong hydrochloric acid into a solid yellow body which separates, and a blue substance which remains dissolved. The latter turns yellow when the hydrochloric acid is neutralised.—4. The yellow body separated by hydrochloric acid, if boiled for a few minutes in an open vessel with a small quantity of potash, soda, or baryta, acquires the property of turning blue in contact with acids.—5. The green parts of plants always contain these two yellow substances in addition to chlorophyll; and the young shoots of various species of spindle-tree (*Euonymus*) contain only these two yellow bodies, without the smallest trace of chlorophyll.—6. The brown substance separated from an alcoholic solution of chlorophyll on addition of oxalic acid, is rich in nitrogen, and is identical with the substance described and analysed by Morot (i. 922).—7. The solutions of this brown substance have a high degree of dichroïsm, which is not exhibited by those of the yellow substance.—8. The solutions of the brown substance treated with caustic alkalis in contact with the air, assume an orange-red colour, which again disappears in consequence of absorption of oxygen, and gives place to a pure green colour.—9. Certain metallic oxides, especially zinc-oxide dissolved in potash, accelerate the oxidation of the brown substance. The splendid green colour thus produced may be precipitated on textile fabrics, but it is of no use as a dye, being quickly destroyed by light and air.—10. Leaves of plants which are coloured red, brown, or violet over their whole surface, are green in spring and yellow in autumn in the parts below the surface. This is easily shown by means of a mixture of sulphurous acid and ether, which dissolve the colouring matter of the superficial cells, and bring to light the green or yellow colour of those in the interior of the tissue.

Pfaundler (*Ann. Ch. Pharm.* cxv. 37; *Jahresb.* 1860, p. 531) adopts the opinion formerly expressed by Hlasiwetz (*Jahresb.* 1859, p. 527) that the colours of plants depend on the presence of quercitrin, æsculin, and other analogous principles, which produce various shades of colour under the influence of alkalis, air, and salts of iron. In support of the assertion of Verdeil (*ibid.* 1851, p. 574) that the formation of leaf-green is essentially connected with the presence of iron, Pfaundler adduces a series of experiments by Salm-Horstmar (*Ueber die Nahrung der Pflanzen*, Braunschweig, 1856) showing that in plants grown in artificial soils not containing iron, the colour of the green parts was very pale, or even quite destroyed, whereas when iron was present the normal green colour was developed. Chlorophyll prepared by heating the juice of grasses to the boiling point, exhausting the coagulum with alcohol, distilling off the alcohol, dissolving the residual dark green jelly in hydrochloric acid, precipitating the filtered solution with hot water, and washing the green flocks thereby separated, forms when dry a dark blue powder, producing with alcohol and ether dark-coloured solutions, nearly blood-red by reflected light, yellow-green by transmitted light; with carbon bisulphide a brown-yellow, with hydrochloric acid a grass-green solution; soluble also in dilute potash, but separated by strong potash-ley in resinous lumps; not resolvable like quercetin, or reducible like indigo. It was free from nitrogen, gave 0·9 p. c. ash, in which iron could be distinctly detected, and gave by analysis 60 p. c. carbon and 6·4 hydrogen, calculated for the substance free from ash. Pfaundler further remarks that there may be several kinds of chlorophyll, and that the assumption of a single chlorophyll does not rest on very good grounds.

According to Phipson (*Compt. rend.* xlvii. 912), green leaves immersed in strong sulphuric acid assume a yellow autumnal colour; after prolonged contact, the yellow changes to emerald-green, and afterwards ulmic substances are formed. Yellow autumnal leaves immersed for a few seconds in sulphuric acid become emerald-green and afterwards brown.

According to Sachs (*Jahresb.* 1859, p. 561), vegetable plasma contains a colourless substance, *leucophyll*, possessing the constitution of leaf-green, and awaiting only a final chemical impulse to convert it into green chlorophyll. This impulse is given, not so much by light as by oxygen, in the active state, or rendered active by the influence of light. The still colourless cells of plants, in the state in which they would rapidly turn green on exposure to light, are instantly coloured green if immersed in sulphuric acid, whereas cells not in a state to be turned green by light are not thus altered by sulphuric acid.

According to Jodin (*Compt. rend.* lix. 857), solutions of chlorophyll, even in presence of alkali, retain their colour in the dark, whereas in sunlight they are decolorised in a few days, absorbing at the same time a quantity of oxygen equal to 0·72 of the weight of the colouring matter, and giving off carbonic acid. According to H. Vohl (*J. pr. Chem.* xcv. 219), the chloroform of horse-chestnut leaves is not decomposed by putrefaction of the leaves going on for several years.

CHLOROPICRIN. $C(NO^2)Cl^3$. *Trichloronitromethane. Nitrochloroform.*—Formed by distilling chloral or metachloral with strong nitric acid, or with a mixture of nitric and sulphuric acids; also by distilling a mixture of methyl alcohol and sulphuric acid over a mixture of potassium nitrate and sodium chloride. These two modes of formation show that chloropicrin belongs to the methyl group (Kekulé, *Ann. Ch. Pharm.* cvi. 144). According to S. Priestley (*Chem. News*, ix. 3), chloropicrin may be prepared by adding nitric acid by small portions to a cooled pasty mixture of methyl alcohol and chloride of lime, and subjecting the whole to distillation. The mixture of chloropicrin, chloroform, and methyl alcohol which condenses in the receiver may be separated by fractional distillation, the chloropicrin, which is the least volatile, remaining behind.

For preparing chloropicrin in large quantity, Hofmann (*Ann. Ch. Pharm.* cxxxix. 107) mixes 45 kilo. of recently prepared chloride of lime, stirred up to a thick paste with cold water, in a capacious earthenware still surrounded by cold water, with a saturated solution of 45 kilo. of picric acid heated to 30°. A violent reaction takes place after a few minutes, and the greater part of the chloropicrin produced is driven over into the receiver, which should be connected by a conducting tube with the chimney to prevent the escape of the pungent vapours of chloropicrin. As soon as the first action is over, the water-bath is heated to boiling, to distil over the remainder of the chloropicrin. The chloropicrin thus obtained amounts to 114 p. c. of the picric acid used.

Chloropicrin boils at 112° (Hofmann).

Reactions.—1. Chloropicrin treated with *iron-filings* and *acetic acid*, or with ferrous sulphate and excess of potash, is converted into methylamine:

$$CNO^2Cl^3 + 12H = CH^5N + 3HCl + 2H^2O$$

(Geisse, *Ann. Ch. Pharm.* cix. 282; *Jahresb.* 1859, p. 437). See also the same paper for the action of alkaline sulphites on chloropicrin.

2. Heated to 100° for 24 hours with fuming *hydriodic acid*, chloropicrin is decomposed in the manner represented by the equation:

$$C(NO^2)Cl^3 + 6HI = NH^3 + CO^2 + 3HCl + 3I^2$$

(E. J. Mills, *Chem. Soc. J.* [2] ii. 153).

3. By heating with *sodium ethylate* (sodium and absolute alcohol), it is converted into ethylic orthocarbonate (Bassett, *Chem. Soc. J.* [2] iv. 238):

$$C(NO^2)Cl^3 + 4C^2H^5ONa = 3NaCl + NO^2Na + C(C^2H^5)^4O^4.$$

4. Chloropicrin heated with 9 mol. of fused *potassium acetate* and *alcohol* to 100°, is easily decomposed, yielding ethyl acetate, together with chloride, nitrite, carbonate, and acid acetate of potassium (Bassett, *Chem. Soc. J.* [2] ii. 31):

$$C(NO^2)Cl^3 + 9C^2H^3O^2K + 3C^2H^6O = 3(C^2H^3O^2.C^2H^5) + 3KCl + NO^2K \\ + CO^3K^2 + 3(C^2H^3O^2K.C^2H^4O^2).$$

5. Chloropicrin heated with *potassium cyanide*, alcohol, and water, is converted into dicyano-nitro-chloromethane, $C(NO^2)Cl(CN)^2$. This compound is soluble in water, alcohol, ether, and chloroform, very easily decomposible, and has not been obtained in the separate state, but only in combination with water, and with metallic oxides and salts. Lead acetate added to its aqueous solution forms a precipitate containing $C(NO^2)Cl(CN)^2.3PbO$; with silver nitrate a precipitate is formed consisting of $3C(NO^2)Cl(CN)^2.4NO^3Ag.8H^2O$ (Bassett, *Chem. Soc. J.* [2] iv. 352). For the details of the preparation, which requires particular precautions, we must refer to the original paper.

6. Chloropicrin heated with *ammonia* in alcoholic solution is converted into guanidine-hydrochloride (Hofmann, *Chem. Soc. J.* [2] iv. 249; *Zeitschr. f. Chem.* [2] iv. 721):

$$C(NO^2)Cl^3 + 3NH^3 = CH^5N^3.HCl + 2HCl + NO^2H.$$

CHLOROSULPHOFORM. $C^2Cl^2S^3$.—W. N. Hartley (*Chem. Soc. J.* [2] v. 23) obtained this compound by treating a mixture of monochloride, dichloride, and trichloride of carbon with an alcoholic solution of potassium sulphydrate. On precipitating the product with water, and distilling the washed product, the chlorosulphoform remained in the residue, together with sulphur, and was purified by repeated crystallisation from alcohol. It crystallises in needles, has an unpleasant odour, melts at about 250°, but begins to sublime at a lower temperature. It is insoluble in water, slightly soluble in alcohol and ether, more freely in carbon bisulphide, chloroform, the liquid chlorides of carbon, and oil of turpentine. When heated for several hours in sealed tubes with nitric acid, it yields sulphuric acid and a sulphuretted compound crystallising in white scales. It is produced in the above reaction entirely from the carbon monochloride, by direct addition of sulphur at the moment that the latter is set free (Hartley). As the so-called carbon monochloride, C^2Cl^2, has been shown to be identical with hexchlorobenzene, C^6Cl^6 (p. 267), the formation of chlorosulphoform probably takes place in the manner shown by the equation $C^6Cl^6 + 9S = 3C^2Cl^2S^3$.

CHOLESTERIN. $C^{26}H^{44}O$.—This substance occurs, together with protagon (iv. 737), as an essential constituent of the nervous tissue, of the yolk of egg, of the seminal fluid, and of the red and colourless corpuscles of the blood (Hoppe-Seyler, *Med.-chem. Unters.* i. 140; *Jahresb.* 1866, p. 744). It has been found by Tolmatscheff (*Med.-chem. Unters.* i. 272) in human milk, to the amount of 0·0318 p. c.; by Marcet (*Ann. Ch. Phys.* [3] lix. 91) in the spleen, and abundantly in the excrements of the crocodile; by Hoppe-Seyler (*Jahresb.* 1863, p. 654) in guano; and by Piccolo a. Lieben (*Zeitschr. f. Chem.* iv. 646) in the *corpus luteum* of the cow. It is also found in vegetable substances, viz. in peas, and in certain fixed oils (Benneke, *Ann. Ch. Pharm.* cxxxii. 249; Lindenmeyer, *J. pr. Chem.* xc. 321); in the fat of wheat-gluten and of rye (Ritthausen, *Jahresb.* 1863, p. 544; *Zeitschr. f. Chem.* [2] iv. 314); in that of barley (Lentner, *ibid.* 664); in maize-seeds; in the young shoots (eyes) of roses, and in wine-yeast (Hoppe-Seyler, *Jahresb.* 1866, pp. 698, 744).

To prepare cholesterin from peas, the bruised seeds (5 lb.) are digested with an equal weight of alcohol of 94 p. c. at 36°–40°, and the extract, after standing for 24 hours, is filtered and evaporated. The brown-yellow glutinous residue (which exhibits with sugar-water the forms of myelin (iii. 1068) is dissolved in about 400 c.c. of water, and the solution is boiled with litharge (1 lb.) till the supernatant liquid becomes clear. The separated lead precipitate is then exhausted, first with cold and then with boiling alcohol, and the alcoholic solution is freed from lead by hydrogen sulphide. The filtrate left to cool yields crystals of cholesterin, a further quantity of which is deposited as the alcohol evaporates. The portion still remaining in solution may be obtained by evaporating off the whole of the alcohol and boiling the aqueous solution of the residue with baryta-water; boiling the flocculent barium-compound which separates, with alcohol; and leaving the filtrate, freed from barium by sulphuric acid, to crystallise: 5 lb. of peas thus treated yield 1·5 grm. of cholesterin, identical in every respect with that obtained from animal substances (Benneke). Lindenmeyer (*J. pr. Chem.* xc. 321) exhausts the bruised peas repeatedly with alcohol containing ether; agitates the aqueous solution of the extract several times with ether; boils the residue left on evaporating the ether with alcoholic potash for an hour, ultimately evaporating to dryness; and repeatedly agitates the aqueous solution of the residue with ether. On evaporating the ether, the chloresterin remains, and may be freed from a yellow colouring matter by washing with cold alcohol. Lindenmeyer found that the dry substance of unripe peas, amounting to 36·6 to 38 p. c., contains from 0·024 to 0·026 p. c. cholesterin, whereas the dry substance of ripe peas, amounting to 84 to 89 p. c., contains from 0·051 to 0·059 p. c. cholesterin—consequently that the amount of cholesterin in peas increases considerably as they ripen.

The following process is given by Hoppe-Seyler for the simultaneous detection and estimation of cholesterin, protagon, and saponifiable fats in animal and vegetable substances: The substance is repeatedly exhausted with its own volume or with several volumes of ether; the clear decanted or filtered extracts, quite separated from the aqueous solution, are distilled over the water-bath; and the dried residue is weighed. Part or the whole of this residue is then boiled for several hours with an excess of clear concentrated alcoholic potash, the alcohol finally evaporated, the residue dissolved in water, and the solution repeatedly agitated with ether. This ethereal extract usually contains the cholesterin almost pure. In the contrary case, the residue, while still warm, must be shaken up with dilute potash, and after cooling again treated with ether, which then does not take up any of the soaps produced by the action of the alkali, unless the quantity of water or alkali present is deficient. The soap-solution freed from the cholesterin is strongly supersaturated with hydrochloric acid and repeatedly agitated with ether; the united ethereal extracts are distilled off; and the dried residue is weighed. The acid aqueous solution (freed from the fatty acids by ether) is evaporated to dryness in a platinum dish; the residue is fused with soda and nitre; and the aqueous solution of the fused mass, after acidulation with nitric acid, is precipitated by a solution of ammonium molybdate in nitric acid. In this precipitate, collected after standing for 24 hours, the phosphorus is estimated by solution in ammonia and precipitation with ammoniacal magnesia-solution, and from this the amount of protagon, $C^{116}H^{241}N^4PO^{22}$, is calculated. The quantity of the saponifiable fats is found by deducting the weights of the protagon and cholesterin from the total weight of the original ethereal extract. Respecting the quantities of cholesterin thus found in the serum and corpuscles of blood, see p. 351.

Cholesterin rotates a ray of polarised light to the left, its specific rotatory power being −27·5° for red, and −34·5° for yellow light (Hoppe-Seyler, *Jahresb.* 1862, p. 567). Lindenmeyer (*ibid.* 1863, p. 542) has made the following determinations of the lævogyrate power of cholesterin for the different fixed lines in the spectrum:

B	C	D	E	b	F	G
20·63°	25·54°	31·59°	39·91°	41·92°	48·65°	62·37°.

The rotatory power of cholesterin affords the means of quickly estimating its proportion in oil of almonds and cod-liver oil, and of distinguishing these oils from others which do not possess the lævorotatory power (*e.g.* poppy, sesame, olive,* rape, &c.). For the estimation of cholesterin in peas, however, the chemical method above given must be resorted to, inasmuch as the peas likewise contain a dextrogyrate substance not yet isolated; 1 pt. of cholesterin dissolves in 6·65 pts. of *chloroform* at 20° (Lindenmeyer).

When a small quantity of cholesterin is evaporated at a gentle heat with a drop of *nitric acid*, a yellow spot is left, which turns red when touched with a drop of ammonia; and the red colour thus produced is not essentially altered by subsequent addition of a fixed alkali—a character which distinguishes this reaction from the similar one produced with uric acid. When cholesterin is treated with a mixture of 2 or 3 vol. strong *hydrochloric* or *sulphuric acid* and 1 vol. of moderately dilute solution of *ferric chloride*, and the whole is evaporated to dryness, a reddish-violet residue is obtained, changing to blue-violet at a somewhat higher, and to dull grey at a still higher temperature. This reaction, which is likewise produced with auric or platinic chloride, or with potassium dichromate and hydrochloric acid, is not exhibited by the colouring matter or any other constituent of the bile (H. Schiff, *Ann. Ch. Pharm.* cxv. 313).

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* According to Benneke, olive oil contains cholesterin.

Cholesterin Dibromide, $C^{26}H^{44}OBr^2$, is formed by the action of bromine on cholesterin, both dissolved in carbon bisulphide, and separates on leaving the solution to evaporate. After recrystallisation from hot ether-alcohol, it forms white needle-shaped crystals, insoluble in water, slightly soluble in alcohol, easily in ether. It melts and chars when heated, and is reconverted into cholesterin by sodium-amalgam. The same compound appears to be formed by the action of bromine on cholesterin in ethereal solution (Wislicenus a. Moldenhauer, *Ann. Ch. Pharm.* cxlvi. 175).

CHOLESTERIC ETHERS.—*Sodium cholesterate*, $C^{26}H^{43}NaO$, is formed, with evolution of hydrogen, when sodium is added to a saturated solution of cholesterin in petroleum (previously purified with sodium). The solid compound which separates melts at 150°, decomposes at 180°, and crystallises from petroleum, or from a strongly cooled solution in anhydrous chloroform, in silky needles which are slowly decomposed by water, more quickly by alcohol. When heated for some days with 1 mol. *ethyl iodide* to 100°, it yields, together with sodium iodide, a body crystallising from ether in tables melting at 141°, and apparently consisting, not of ethyl cholesterate or cholesteryl ethylate, but of cholesteryl oxide. By treating sodium cholesterate with cholesteryl chloride (*infra*) at 100°, another body is produced, insoluble in alcohol, and crystallising from ether like cholesterin, but melting at 71°. *Cholesteric acetate*, $C^{26}H^{43}(C^2H^3O)O$, produced by the action of acetyl chloride on sodium cholesterate, crystallises from ether (after the excess of cholesterin has been removed by boiling alcohol) in moss-like crystals, which are decomposed by boiling alcoholic potash, yielding potassium acetate.

Cholesteryl Chloride, $C^{26}H^{43}Cl$, is produced by the action of phosphorus pentachloride on cholesterin, and purified by pressure, boiling with water, and crystallisation from ether and alcohol. It dissolves readily in ether, sparingly in alcohol, melts at 100°, and exhibits just before solidification a bright violet colour by reflected, yellowish-green by transmitted light. It is not decomposed by aqueous potash, but with boiling alcoholic potash it yields potassium chloride and cholesterin (Planer, *Ann. Ch. Pharm.* cxviii. 25; Lindenmeyer, *loc. cit.*).

CHOLINE or NEURINE. $C^5H^{15}NO^2 = \left.\begin{matrix}C^2H^4OH\\(CH^3)^3\end{matrix}\right\}N.OH$ (Strecker, *Compt. rend.* lii. 270; *Ann. Ch. Pharm.* cxxxiii. 353; *Zeitschr. f. Chem.* [2] iv. 218, 438. Liebreich, *Ann. Ch. Pharm.* cxxxiv. 29. Baeyer, *ibid.* cxl. 306. Dybkowsky, *J. pr. Chem.* c. 163; *Jahresb.* 1867, p. 493. Wurtz, *Ann. Ch. Pharm. Suppl.* vi. 116; *Compt. rend.* lxv. 1015; lxviii. 1434; *Zeitschr. f. Chem.* [2] iv. 169; v. 481).—Strecker in 1861 obtained from pigs' bile, and afterwards from ox-bile, a base which he called choline. Liebreich in 1865, by decomposing protagon, the chief constituent of nervous tissue (iv. 737), with alkalis, obtained a similar base, which he termed neurine; and these two products were afterwards shown by Baeyer, Dybkowsky, and Strecker to be identical. The rational formula of this base was discovered by Baeyer, and confirmed by Wurtz, who has produced it synthetically.

Preparation: 1. *From Bile.*—The alcoholic solution of inspissated bile is precipitated by ether; the portion remaining dissolved is boiled (after the ether and alcohol have been driven off) for twelve to twenty-four hours with baryta-water; the excess of baryta is removed by carbonic acid; the strongly concentrated filtrate is mixed with absolute alcohol; and the alcoholic solution separated from the resulting precipitate is neutralised with hydrochloric acid. Taurine then separates out, and the liquid filtered therefrom gives with platinic chloride a yellow amorphous precipitate of choline platinochloride, which crystallises from water (together with more sparingly soluble octohedral crystals) in orange-red six-sided tables containing $(C^5H^{14}NOCl)^2.PtCl^4$ (Dybkowsky).

2. *From Brain.*—Fresh ox-brain is rubbed through a fine sieve; the pulp is exhausted with ether; the residue of the ethereal solution is boiled with baryta-water; and the preparation is completed as above. The crystals of the neurine platinochloride thus obtained have the same form and composition as those of the choline salt (Dybkowsky). According to Claus a. Keesé (*Zeitschr. f. Chem.* [2] iv. 46), choline appears to be likewise identical [or isomeric?] with sincaline (v. 311).

3. *By Synthesis.*—By heating trimethylamine (5 grms.) with glycolic chlorhydrin, (10 grms.) for 24 hours to 100° in a sealed tube, which then becomes filled with deliquescent prismatic crystals of trimethyl-oxethylammonium chloride, identical in composition with neurine chloride:

$$(CH^3)^3N + C^2H^4(OH)Cl = \left.\begin{matrix}C^2H^4(OH)\\(CH^3)^3\end{matrix}\right\}N.Cl$$

This salt dissolves abundantly in boiling alcohol, and separates partially on cooling from a very concentrated solution. The solution gives with auric chloride a yellow crystalline precipitate of the *aurochloride* $(CH^3)^3(C^2H^4OH)NCl.AuCl^3$, which exhibits under the microscope the same form (rhombic laminæ) as the gold salt prepared with neurine from brain. The hydrate $(CH^3)^3(C^2H^4OH)NOH$, obtained by treating the chloride with moist silver oxide, is a syrupy liquid which decomposes when heated, giving off an ammoniacal odour (Wurtz).

From these results it appears that choline or neurine has the constitution of trimethyl-oxethyl-ammonium hydrate. The same conclusion had previously been arrived at by Baeyer, who found that a concentrated solution of neurine hydrochloride, heated with strong hydriodic acid and a little amorphous phosphorus, yields an iodide, $C^5H^{13}NI^2$ or $C^5H^{12}IN.HI$, perfectly analogous in its reactions to the bromide $C^5H^{13}NBr^2$, which Hofmann obtained by treating trimethylamine with ethylene bromide, and producible from the same bromide by treatment with silver oxide and then with hydriodic acid. A solution of the bromide in hot hydriodic acid yields on cooling, crystals of the bromiodide $C^5H^{13}NBrI$; the latter treated with silver chloride yields the corresponding bromochloride; and this compound treated with platinic chloride yields the double salt $(C^5H^{13}NBrCl)^2PtCl^4$, identical with that obtained by Hofmann (iii. 1001).

Amyl-glycolic chlorhydrin heated with excess of ammonia yields the *chloride of hydroxamyl-ammonium*, isomeric with choline chloride:

$$C^5H^{10}(OH)Cl + NH^3 = \left.\begin{matrix}C^5H^{10}OH\\H^3\end{matrix}\right\}N.Cl;$$

and ethyl-glycolic chlorhydrin heated with triethylamine yields the *chloride of hydroxethyl-triethylammonium*, homologous with choline chloride:

$$C^2H^4(OH)Cl + (C^2H^5)^3N = \left.\begin{matrix}C^2H^4OH\\(C^2H^5)^3\end{matrix}\right\}N.Cl$$

Wurtz (*Compt. rend.* lxviii. 1434; *Zeitschr. f. Chem.* [2] v. 481).

CHOLOÏDIC ACID. According to Hoppe-Seyler (*J. pr. Chem.* lxxxix. 83), the substance thus designated, which is produced by boiling bile with acids, is nothing but a mixture of cholic acid, dyslysin, and cholonic acid, perhaps also containing undecomposed glycocholic and taurocholic acids.

CHONDRIN. Optical rotatory power, in weak alkaline solution = −213·5°; after addition of an equal colume of soda-ley = −552°; and after addition of an equal volume of water = −281° (J. de Bary, *Med.-chem. Unters.* i. 71; *Jahresb.* 1866, p. 715). Fischer a. Bödeker (*Ann. Ch. Pharm.* cxvii. 1) found that pure rib-cartilage boiled with strong hydrochloric acid, yields a sugar, which reduces cupric oxide in alkaline solution, and is capable of fermenting with yeast: hence they inferred that chondrin contains a glucoside. De Bary, who designates the sugar thus obtained as chondroglucose, finds that it differs from grape-sugar in possessing lævogyrate power (not varying with the temperature, and, according to one experiment, = −45·5° for yellow light); further, in being uncrystallisable or very difficult to crystallise; also in being difficultly fermentable, and splitting up thereby, like melitose, into a fermentable and a nonfermentable (lævogyrate) sugar.

Otto (*Zeitschr. f. Chem.* [2] iv. 628) has confirmed the observation formerly made by Hoppe-Seyler (*J. pr. Chem.* lvi. 129) that chondrin yields considerable quantities of leucine when boiled with sulphuric acid, but does not yield glycocine by boiling either with sulphuric acid or with baryta-water.

CHROMIUM. Deville obtains this metal in the fused state by igniting a mixture of chromic oxide and sugar charcoal in a lime crucible intensely heated in a portable blast-furnace. The metal thus prepared is shining, has a steel-grey colour, a specific gravity of 6, and is hard enough to scratch glass. J. Loughlin (*Zeitschr. f. Chem.* [2] v. 113) prepares metallic chromium by exposing a mixture of chromic oxide and potassium cyanide to a white heat in a covered porcelain crucible. A solution of chromic chloride or other chromic salt treated with sodium-amalgam, yields an amalgam of chromium, which when heated in as tream of hydrogen, leaves metallic chromium in the form of a pulverulent sponge (Vincent, *Phil. Mag.* [4] xxiv. 328; Roussin, *Bull. Soc. Chim.* [2] vi. 23).

Detection and Estimation.—Chromic salts when very much diluted are somewhat difficult to distinguish from salts of nickel. In either case ammonium sulphydrate produces no precipitate, but merely colours the liquid more or less dark brown. But on adding a few drops of hydrochloric acid to a small quantity of the solution in a porcelain capsule, and leaving the liquid to evaporate, the residue, if nickel is present, turns first blue, then green, and finally yellow; but in the case of chromium, the sides of the capsule exhibit successively a blue, a violet, and a green colour, and finally a residue is left of a fine carmine-red colour, which is quickly decomposed by water, but is insoluble in cold alcohol and ether, and permanent; when strongly heated, it gives off white vapours and leaves a green residue; with lime it gives off ammonia. This reaction probably depends on the formation of a roseo-chromic salt analogous to the roseo-cobaltic salts (C. Husson, *Zeitschr. f. Chem.* [2] iv. 569).

Tincture of guaiacum is an extremely delicate test for chromic acid. Of a solution containing only 0·00004 grm. of chromic anhydride in a cubic centimetre, $\frac{1}{10}$ c.c. added to a few drops of guaiacum tincture (1 pt. of the resin to about 100 pts. of 60 p. c. alcohol) in a porcelain capsule, immediately produces a deep blue colour. This reaction serves to demonstrate the solubility of lead chromate and barium chromate in distilled water (Schiff, *Ann. Ch. Pharm.* cxx. 208; *Jahresb.* 1861, p. 253).

Chromic oxide is easily and quickly oxidised to chromic acid by a mixture of nitric acid and potassium chlorate. Even chrome iron ore and strongly ignited chromic oxide are oxidised in this manner more quickly than by the ordinary fusion process. The chromium is then easily estimated in the form of barium chromate (A. H. Pearson, *Zeitschr. f. Chem.* [2] v. 661).

For other methods of analysing chrome-ores see Genth, *Chem. News*, vi. 30; O'Neill, *ibid.* v. 199.

W. Gibbs (*Sill. Am. J.* [2] xxxix. 58) describes a method of separating chromic oxide from the oxides of iron, manganese, cobalt, nickel, and zinc, also from alumina and magnesia, founded on the conversion of chromic oxide into chromic acid by the action of chlorine, bromine, or dioxide of lead in alkaline solution. When chlorine or bromine is used, the solution is ultimately neutralised with acetic acid; and when sulphuric acid is absent, the chromic acid is precipitated by barium acetate. It is better however to pass chlorine into the *hot* neutral chromic solution mixed with sodium acetate, and neutralise the liberated acid from time to time with sodium carbonate. Alumina and ferric oxide are then separated at the boiling heat, while the other oxides remain dissolved, together with the chromic acid, which may be separated as lead or barium salt.

For the volumetric estimation of chromium in chromates, C. Rube (*J. pr. Chem.* xcv. 53) makes use of the conversion of potassium ferrocyanide into ferricyanide by the action of chromic acid:

$$6\overset{\prime\prime}{\mathrm{Fe}}\mathrm{K}^4\mathrm{Cy}^6 + 2\mathrm{CrO}^3 = \mathrm{Cr}^2\mathrm{O}^3 + 3\mathrm{K}^2\mathrm{O} + 3\overset{\prime\prime\prime}{\mathrm{Fe}}{}^2\mathrm{K}^6\mathrm{Cy}^{12}.$$

The aqueous solution of the chromate (0·3 to 0·7 grm.), acidulated with hydrochloric acid and diluted to 150 c.c., is mixed with a solution of the ferrocyanide containing 40 grms. in a litre, till the whole of the chromic acid is reduced and a slight excess of ferrocyanide is present, which may be known by the production of a greenish instead of a brown colour on treating a drop of the liquid on a porcelain plate with strongly acid ferric chloride. From the number of burette-divisions of the solution used, so many are to be deducted as are required to produce the reaction on ferric chloride in an equal quantity of liquid.

In estimating chromic acid by the iodometric method, Zulkowsky (*Zeitschr. f. Chem.* [2] iv. 661), instead of distilling the chromate with hydrochloric acid, and determining the quantity of chlorine evolved by means of iodine, makes use of the reduction of chromic acid by hydriodic acid in aqueous solution, according to the equation:

$$2\mathrm{CrO}^3 + 6\mathrm{HI} = \mathrm{Cr}^2\mathrm{O}^3 + 3\mathrm{H}^2\mathrm{O} + \mathrm{I}^6.$$

The chromate to be analysed is dissolved in water, mixed with potassium iodide, hydrochloric acid, and starch-paste, and the iodine separated by the reaction is titrated with a $\frac{1}{20}$ normal solution of sodium hyposulphite.

Atomic or Equivalent Value.—Chromium is a hexad element, being sexvalent in the fluoride, CrF^6 (formerly regarded, according to the small atomic weight of chromium, 26, as a trifluoride); in the trioxide, CrO^3; in the chromates, *e.g.* $\left.\begin{matrix}\mathrm{Cr}^{\mathrm{vi}}\\ \mathrm{K}^2\end{matrix}\right\}\mathrm{O}^4$, $\left.\begin{matrix}\mathrm{Cr}^{\mathrm{vi}}\\ \mathrm{Mg}''\end{matrix}\right\}\mathrm{O}^4$; in chromyl dichloride, $\mathrm{CrO}^2\mathrm{Cl}^2$, &c. In the chromic salts it is quadrivalent, these compounds, however, always containing two atoms of chromium, linked together so as to form a sexvalent group, like the two atoms of carbon in ethane, $\mathrm{C}^2\mathrm{H}^6$: thus chromic chloride = $\mathrm{Cr}^2\mathrm{Cl}^6$; chromic oxide, $\mathrm{Cr}^2\mathrm{O}^3$; chromic sulphate, $\mathrm{Cr}^2(\mathrm{SO}^4)^3$, &c. In the chromous compounds it is bivalent, *e.g.* CrCl^2, CrO, &c.

Wanklyn (*Phil. Mag.* [4] xxix. 313) regards chromium as quadrivalent in all its compounds, and represents these compounds by formulæ of which the following may be taken as examples:

$\begin{array}{l}CrCl^2\\ \Vert\\ CrCl^2\end{array}$	$\begin{array}{l}CrCl^3\\ \vert\\ CrCl^3\end{array}$	$Cr\left\{\begin{matrix}Cl^2\\(O^2)''\end{matrix}\right.$	$Cr\left\{\begin{matrix}(OK)^2\\(O^2)''\end{matrix}\right.$
Chromous chloride.	Chromic chloride.	Chlorochromic acid.	Neutral potassium chromate.

These formulæ are based on the analogy of chromic chloride to ferric chloride, on its boiling point, and on the boiling point and vapour-density of chlorochromic acid.

Chromic Oxysalts. Siewert (*Ann. Ch. Pharm.* cxxvi. 86; *Jahresb.* 1863, p. 223) has made observations on the variations of colour in chromic salts, tending to confirm the views of Krüger and Löwel (i. 950), that these changes of colour are due to the formation of compounds containing different proportions of base and acid.

H. Schiff (*Ann. Ch. Pharm.* cxxiv. 165; *Jahresb.* 1862, p. 151) has made the following observations on basic and polyacid salts of chromium. The dark green saturated solution of chromic hydrate in dilute sulphuric acid, evaporated at 50°–60°, leaves a similarly coloured soluble basic salt consisting of $\left.\begin{matrix}(Cr^2)^{vi}\\(SO^2)^2\\H^2\end{matrix}\right\}O^6.2H^2O$ or $(Cr^2)^{vi}\left\{\begin{matrix}(SO^4)^2\\(HO)^2\end{matrix}\right..2H^2O$. The solution of this salt in a small quantity of water is neutral, and may be boiled without decomposition; but on adding more water, a still more basic salt is precipitated; and if this precipitate be dissolved in a very small quantity of hydrochloric acid, the solution much diluted, and boiled for a few hours, decanted after cooling from a few flocks which may have separated, and incompletely precipitated by ammonia, light blue flocks are obtained, consisting of the salt $Cr^2\left\{\begin{matrix}SO^4\\(HO)^4\end{matrix}\right..2H^2O$.

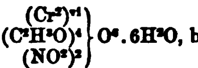
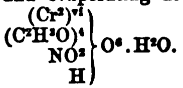
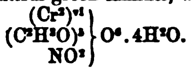
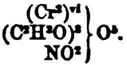
A *chromic hydroxychloride*, $(Cr^2)^{vi}\left\{\begin{matrix}(HO)^4\\Cl^2\end{matrix}\right.$, is obtained by digesting the solution of chromic chloride for several days with excess of chromic hydrate, evaporating the resulting solution, and drying at 100° (Schiff, *Ann. Ch. Pharm.* cxxiv. 171). This compound was also obtained in the hydrated state, $Cr^2(HO)^4Cl^2.H^2O$ [or $Cr^2O^2Cl^2.3H^2O$], by Peligot (i. 954). With a smaller quantity of chromic hydrate the compound $Cr^2(HO)^2Cl^4$ is produced.

Polyacid Salts.—The sulphate $Cr^2\left\{\begin{matrix}SO^4\\(HO)^4\end{matrix}\right.$ dissolves in nitric acid, forming a dark green liquid, which when evaporated at 80°–90° and dried at 100°, consists of *chromic sulphatotetranitrate*, $(Cr^2)^{vi}\left\{\begin{matrix}(SO^4)''\\(NO^3)^4\end{matrix}\right.$ or $\left.\begin{matrix}(Cr^2)^{vi}\\(SO^2)''\\(NO^2)^4\end{matrix}\right\}O^6$. It dissolves completely in water, the solution being yellow-green in the cold, green at the boiling heat, and having an acid reaction. With barium chloride it forms only a slight cloud at ordinary temperatures, but a more copious precipitate at the boiling heat. *Chromic disulphatonitrate*, $Cr^2\left\{\begin{matrix}(SO^4)^2\\(NO^3)^2\end{matrix}\right.$, is obtained by saturating the diacid sulphate with nitric acid. It is a green, tumefied, hygroscopic, saline mass, the solution of which has an acid reaction and astringent taste, and in other respects resembles that of the preceding salts.

Chromic diacetotetrachloride, $Cr^2\left\{\begin{matrix}(C^2H^3O^2)^2\\Cl^4\end{matrix}\right..4H^2O$, is obtained by dissolving the basic chloride $Cr^2(HO)^2Cl^4$ in strong acetic acid; the *diacetodisulphate*, $Cr^2\left\{\begin{matrix}(C^2H^3O^2)^2\\(SO^4)^2\end{matrix}\right.$, by dissolving the corresponding basic sulphate in acetic acid.

By dissolving the disulphate in cold hydrochloric acid, and evaporating at about 50°, a green amorphous mass is obtained, consisting of *chromic disulphatodichloride*, $Cr^2\left\{\begin{matrix}(SO^4)^2\\Cl^2\end{matrix}\right..2H^2O$. By dissolving the dihydroxytetrachloride, $Cr^2(HO)^2Cl^4$, in nitric acid, the *dinitratotetrachloride*, $Cr^2\left\{\begin{matrix}(NO^3)^2\\Cl^4\end{matrix}\right.$, is obtained, as a hygroscopic mass consisting o shining laminæ. The tetrahydroxydichloride, $Cr^2(HO)^4Cl^2$, dissolved in a small quantity of nitric acid, yields the *dinitratodichloride*, $Cr^2\left\{\begin{matrix}(NO^3)^2\\(HO)^2\\Cl^2\end{matrix}\right.$, as a light green, porous, hygroscopic mass, which crumbles to powder when stirred (Schiff).

The chromic acetates obtained by Schiff are described under ACETATES (p. 9).

Schützenberger has obtained a *chromic acetonitrate*,  $\left.\begin{matrix}(Cr^2)^{vi}\\(C^2H^3O)^4\\(NO^2)^2\end{matrix}\right\}O^6.6H^2O$, by mixing chromic nitrate and acetate in the required proportions and evaporating under the air-pump. A similar salt, crystallising in green laminæ or granules, is obtained on mixing 4 to 5 mol. of normal chromic acetate with 1 mol. of normal chromic nitrate, and evaporating at the boiling heat. When dried at 110° it has the composition  $\left.\begin{matrix}(Cr^2)^{vi}\\(C^2H^3O)^4\\NO^2\\H\end{matrix}\right\}O^6.H^2O$. It dissolves easily in hot glacial acetic acid, and the solution on cooling yields beautiful green laminæ, which after drying in a vacuum or at 100° have the composition  $\left.\begin{matrix}(Cr^2)^{vi}\\(C^2H^3O)^3\\NO^2\end{matrix}\right\}O^6.4H^2O$. Heated to 200°, these crystals give off water and acetic acid; at a higher temperature nitrous vapours are evolved, and the pulverulent mass assumes a yellow-brown colour. In this state it forms with water a dirty-brown solution, in which chromic acid may be detected. But at about 350° a somewhat violent reaction takes place, attended with evolution of gas, and there remains a light green, very finely divided, light powder, pyrophoric when heated. When very carefully prepared by heating the above-mentioned acetonitrate with the vapour of boiling mercury, it has the composition  $\left.\begin{matrix}(Cr^2)^{vi}\\(C^2H^3O)^2\\NO^2\end{matrix}\right\}O^5$. This powder immediately takes up water, with rise of temperature, and is converted into a homogeneous deep green paste, which might perhaps be used as a pigment. The greater the quantity of water added, the more does this paste swell up, and finally it is converted into a green colloïdal solution, which when mixed with an alkali deposits the whole of the salt. At about 400° the anhydrous powder gives off more acetic acid, without losing the power of uniting with water. At the temperature of boiling sulphur, complete decomposition takes place, anhydrous chromic oxide being left, mixed with charcoal.

Ammoniacal Chromic Salts.—Frémy, by the action of ammonia and ammoniacal salts on metachromic hydrate, obtained salts of a base $Cr^2O^3.8NH^3$, which he called roseochromammonia (i. 951). Ammonio-chromic compounds of different composition have been obtained by Cleve (*J. pr. Chem.* lxxxvi. 47; *Jahresb.* 1862, p. 149). When the grey-green hydrate, precipitated by a slight excess of ammonia from a cold saturated solution of chrome-alum, is digested in a closed vessel with a saturated solution of ammonium chloride in ammonia, till it dissolves with deep rose-red colour, and the resulting solution is exposed to the air, a reddish-violet amorphous powder is precipitated, which dissolves with dark red colour in dilute hydrochloric acid. This solution gradually deposits a bright red crystalline powder, which dissolves in hydrochloric acid, and separates by slow evaporation in well-defined rhombic prisms, consisting of the salt $Cr^2Cl^6.8NH^3.2H^2O$, designated by Cleve as *tetramine-chromic chloride*. The crystals have a deep red colour and vitreous lustre, give off only hygroscopic water at 100°, but decompose at 200° with evolution of ammonia. They dissolve in water, forming a neutral solution which gives off ammonia when boiled, and is easily decomposed by alkalis. This salt forms double salts with platinic chloride and mercuric cyanide. The *platinum salt* $Cr^2Cl^6.8NH^3.2H^2O.PtCl^4$ is a brown-red crystalline powder soluble in hot water. The chloride treated with sulphuric acid yields a *sulphato-chloride* of complex constitution. A *nitrate* is obtained by decomposing the chloride with an equivalent quantity of silver nitrate, in large, apparently hexagonal tables, which dissolve readily in water, are reconverted into the original chloride by hydrochloric acid, and are decomposed by heat into ammonia, ammonium nitrate, and chromic oxide.

Chromium Trioxide or **Chromic Anhydride,** CrO^3, may be prepared by heating barium chromate with a large excess of nitric acid slightly diluted with water; decanting the boiling solution from the barium nitrate which separates, and from the further quantity which is deposited on cooling; distilling off the nitric acid till crystals of chromic anhydride separate out on the sides of the retort; then decanting the non-crystallised liquid, and evaporating it to dryness over the water-bath. By finally drying it over the open fire, with constant stirring, the anhydride is obtained in the form of a powder resembling ignited ferric oxide, almost black while hot, but becoming red again on cooling (Siewert, *Jahresb.* 1862, p. 146).

According to Schafarik (*Wien. Akad. Ber.* xlvii. [2] 256), chromic anhydride melts at a temperature a little below the boiling point of strong sulphuric acid, a small quantity subliming at the same time. It deliquesces slowly on exposure to the air; dissolves without alteration in ether, and separates from the reddish-yellow solution in microscopic crystals. Phosphorus reduces it to chromic chromate (Oppenheim, *Jahresb.* 1864, p. 140).

Chromates. According to H. Schwartz (*Dingl. pol. J.* clxxxvi. 31), chromates are but imperfectly decomposed by sulphuric acid, added in the proportion to form a neutral or acid sulphate. When 2 mol. sulphuric acid are added to a hot solution of 1 mol. potassium dichromate, the liquid on cooling deposits crystals of unaltered dichromate, and afterwards of a mixture of that salt with the tetrachromate (comp. Bolley, *Ann. Ch. Pharm.* lvi. 113). The chromates of lead and barium are only one-fourth decomposed by equivalent quantities of sulphuric acid; the lead-salt requires for decomposition 6 mol. sulphuric acid.

Ammonium Salts.—Siewert (*Jahresb.* 1862, p. 148) confirms the formula of the dichromate, $(NH^4)^2O.2CrO^3$ or $(NH^4)^2CrO^4.CrO^3$, given by Richmond a. Abel (i. 932). Respecting the crystalline form of this salt, see Rammelsberg (*Pogg. Ann.* cxviii. 158; *Jahresb.* 1863, p. 225). The *trichromate*, $(NH^4)^2O.3CrO^3$, obtained by the action of strong nitric acid on the dichromate, forms shining deliquescent crystals of deep garnet-red colour, and generally isomorphous with potassium trichromate. It is resolved by water into chromic acid and the dichromate; becomes black-red at 100°–120°, and detonates sharply at a stronger heat, leaving a greyish-black residue having the form of tea-leaves (Siewert).

Potassium Salts.—The solubility of the *dichromate*, $K^2O.2CrO^3$, in water at various temperatures, has been determined by Alluard (*Ann. Ch. Pharm.* cxxxiii. 292):

$t°$	Salt dissolved by 100 pts. water	$t°$	Salt dissolved in 100 pts. water
0°	4·6	60°	45·0
10	7·4	70	56·7
20	12·4	80	68·6
30	18·4	90	81·1
40	25·9	100	94·1
50	35·0		

A saturated solution boils at 103·4°. Respecting the action of ammonium sulphocyanate on potassium dichromate, see v. 507.

The *trichromate*, $K^2O.3CrO^3$ or $K^2CrO^4.2CrO^3$, is obtained pure and finely crystallised by leaving a solution of the dichromate in excess of aqueous chromic acid to evaporate over oil of vitriol (v. Hauer, *Jahresb.* 1860, p. 161). The *tetrachromate*, $K^2O.4CrO^3$ or $K^2CrO^4.3CrO^3$, is obtained in shining red, thin prismatic laminæ, by leaving a solution of the trichromate in excess of nitric acid over a heated sand-bath, and recrystallising the crusts which separate on cooling, from strong nitric acid (Siewert, *ibid.* 1862, p. 147).

Potassium Chromato-fluoride, $KF.CrO^3$ or $\left.\begin{matrix}(CrO^2)''\\K\end{matrix}\right\}\begin{matrix}O\\F\end{matrix}$ analogous in composition to potassium chromato-chloride (i. 938) and chromium chromato-chloride (p. 456), is obtained by heating pulverised potassium dichromate with excess of concentrated hydrofluoric acid in a platinum dish. It crystallises on cooling in ruby-coloured translucent quadratic octohedrons, with terminal edges of 106° and lateral edges of 115°; becomes dull and reddish-yellow on exposure to the air; cannot be kept in glass vessels; melts easily, when heated, to a dark brown liquid; and decomposes at a red heat in glass vessels, giving off oxygen and silicium fluoride. It dissolves easily in water, especially at the boiling heat, and the solution yields crystals of potassium dichromate, hydrofluoric acid remaining dissolved (Streng, *Ann. Ch. Pharm.* cxxix. 225):

Potassium Sulphato-chromate, $K^2SO^4.CrO^3$ or $\left.\begin{matrix}(CrO^2)''\\(SO^2)''\\K^2\end{matrix}\right\}O^3$, analogous to Bolley's chromo-sulphuric acid (i. 953), is obtained by fusing potassium chromato-chloride, $KCl.CrO^3$, at as low a temperature as possible, with neutral or acid potassium sulphate:

$$K^2SO^4 + KCl.CrO^3 = KCl + K^2SO^4.CrO^3$$

and

$$KHSO^4 + KCl.CrO^3 = HCl + K^2SO^4.CrO^3,$$

It is also found in the mass obtained by heating equivalent quantities of acid sulphate and dichromate of potassium, and is produced in the action of strong sulphuric acid on a concentrated solution of potassium dichromate in excess. It has the same colour as the dichromate, and is decomposed by water into free sulphuric acid, neutral sulphate, and dichromate of potassium, so that it cannot be purified by recrystallisation (Schiff, *Jahresb.* 1863, p. 226).

Sodium Dichromate, $Na^2O.2CrO^3.2aq.$, crystallises in ruby-red or hyacinth-red prisms of 99° 42′ and 80° 18′ (Siewert, *Jahresb.* 1862, p. 147).

Lithium Chromate, $Li^2CrO^4.2H^2O$, forms red-brown rhombic crystals, exhibiting the combination $\infty P . \infty \breve{P}2 . \infty \breve{P}3 . \breve{P}\infty . \bar{P}\infty . \infty \bar{P}\infty . \infty \breve{P}\infty$, the last three faces and $\infty \breve{P}3$ being very subordinate. Axes $a : b : c = 0{\cdot}6619 : 1 : 0{\cdot}4663$. Easily soluble in water. The *dichromate*, $Li^2CrO^4.CrO^3.2H^2O$, obtained by adding chromic or nitric acid to the solution of the neutral salt, and evaporating to a syrup, separates in deliquescent brown-black crystals, having some of their faces curved. *Lithio-ammonic chromate*, $Li(NH^4)CrO^4.2H^2O$, crystallises from a solution of lithium dichromate saturated with ammonia, in slender red-brown deliquescent needles (Rammelsberg, *Pogg. Ann.* cxxviii. 311; *Jahresb.* 1866, p. 160).

Thallium Chromates (v. 754).

Cadmium Chromate (basic), precipitated on mixing the boiling solutions of cadmium sulphate and neutral potassium chromate (which, according to Malaguti a. Sarzeau [i. 933], has the composition $Cd^5Cr^2O^{11} + 8H^2O$), is, according to Frees (*Zeitschr. f. Chem.* [2] vi. 31), a dicadmic salt, $Cd^2CrO^5 + H^2O$ or $2CdO.CrO^3 + H^2O$, part of the chromium being, however, replaced by sulphur, unless the potassium chromate is added in great excess. The same is the case with the basic chromates of copper and zinc.

Calcium Chromate, $CaCrO^4.2H^2O$, prepared by digesting aqueous chromic acid with excess of marble, crystallises by evaporation over sulphuric acid in yellow, apparently quadratic prisms; with quadratoctohedral summits. They assume a cinnabar-red colour when heated, but become yellow again on cooling; give off their water of crystallisation when strongly ignited; require for solution 241·3 pts. water at 14°; but dissolve easily in aqueous chromic acid.

Cobalt Chromate, obtained by precipitating a boiling solution of the sulphate with neutral potassium chromate—to which Malaguti a. Sarzeau assigned the formula $Co^3CrO^6 + 4H^2O$ or $3CoO.CrO^3 + 4H^2O$—is, according to Frees (*Zeitschr. f. Chem.* [2] vi. 31), a dicobaltous salt, $Co^2CrO^5 + 2H^2O$ or $2CoO.CrO^3 + 2H^2O$.

Copper Chromates.—A *tricupric salt*, $3CuO.CrO^3$ or $2CuO.CuCrO^4$, is obtained (mixed with barium sulphate) by prolonged digestion of barium chromate with cupric sulphate at 30°–35°; from its solution in ammonia it is thrown down by nitric acid as a brown precipitate (Viefhaus, *J. pr. Chem.* lxxviii. 431). The same salt is obtained by precipitation of boiling cupric sulphate with neutral potassium chromate; also by digesting cupric carbonate with aqueous chromic acid, or cupric hydrate with potassium dichromate, and subsequent boiling with water: it contains 2 mol. water, which it gives up at about 260°, and recovers on exposure to moist air. This is the only definite basic chromate of copper; the green basic salts described by some authors are merely mixtures containing cupric hydrate or basic sulphate. *Potassio-cupric chromate* is formed, not only by digesting cupric hydrate with potassium dichromate (i. 933), but also by the mutual action of cold solutions of cupric sulphate and potassium dichromate. It is decomposed by boiling water, yielding potassium dichromate and tricupric chromate (Frees, *loc. cit.*).

Mercury Chromates.—The only *basic mercuric chromate* which appears to exist is the *trimercuric salt* (Frees).

Mercuric Chromatosulphide, $HgS.2HgCrO^4$, is obtained by digesting precipitated mercuric sulphide for three or four hours with excess of a solution of recently precipitated mercuric chromate in chromic acid. It must be washed for a short time only, and dried at a temperature not above 30°. It is not attacked by the weaker acids, but sulphuric, nitric, and hydrochloric acid separate the chromic acid and form white compounds. Alkaline solutions change the ochre-coloured salt to orange, and ultimately to black; ammonia quickly converts it into a black powder. The compound detonates with great violence when rubbed, struck, or heated (Palm, *Jahresb.* 1862, p. 222).

Magnesium Salts.—A solution containing equivalent quantities of magnesium sulphate and potassium chromate deposits yellow crystals, having the form of the double sulphates of the magnesium group with $6H^2O$, and containing variable quantities of chromic and sulphuric acids, always however rather less than 1 mol. chromic and rather more than 1 mol. sulphuric acid. A solution containing more than 1 mol. chromic acid and a proportionally smaller quantity of sulphuric acid yields, by crystallisation, the double salt $MgK^2(CrO^4)^2.2H^2O$ (v. Hauer, *Jahresb.* 1860, p. 161).

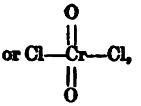
Manganous Chromate (basic), $Mn^2CrO^5 + 2H^2O$, gives off half its water at about 180°, the rest above 300° (Frees).

Nickel Chromate (basic), obtained like the cobalt salt, consists, according to Frees, of $Ni^3CrO^6 + 3H^2O$ or $3NiO.CrO^3 + 3H^2O$.

Zinc Chromates. A *bibasic* zinc chromate, $2ZnO.CrO^3 + 2H^2O$, is formed by adding 2 mol. neutral potassium chromate to 3 mol. zinc sulphate, as a very light pulverulent orange-coloured precipitate, slightly soluble in water. The same salt with 1½ mol. water is obtained by adding chromic acid to water in which basic zinc carbonate is suspended. A *quadribasic salt*, $4ZnO.CrO^3 + 3H^2O$ or $ZnCrO^4 + 3ZnH^2O^2$, is obtained as a fine light-yellow powder, by adding zinc sulphate to an excess of neutral potassium chromate, and freeing the precipitate from potash by washing and repeated boiling with a large quantity of water. A basic *zinco-potassic chromate*, $5ZnO.K^2O.CrO^3 + 6H^2O$, is formed as an orange-yellow pulverulent precipitate on gradually pouring a solution of zinc sulphate into a large excess of neutral potassium chromate (Philippona a. Prüssen, *Ann. Ch. Pharm.* cxlix. 92). According to Frees, the precipitate formed on mixing cold solutions of zinc sulphate and neutral potassium chromate consists of $Zn^4K^2Cr^3O^{14} + 3H^2O$ or $4ZnO.K^2O.3CrO^3 + 3H^2O$, and is resolved by prolonged action of boiling water into potassium dichromate and the quadribasic salt $4ZnO.CrO^3 + 3H^2O$.

An *ammonio-zinc chromate*, $ZnCr^2O^4.4NH^3 + 3H^2O$, crystallising in square tables with octohedral summits, is formed by dissolving the bibasic zinc salt above mentioned in warm aqueous ammonia, precipitating with absolute alcohol, redissolving in ammonia, adding sal-ammoniac and alcohol, again dissolving the precipitate in warm aqueous ammonia, and leaving the solution to cool (Bieler, *Ann. Ch. Pharm.* cli. 223).

Chromic Chromate or *Chromium Dioxide*, $CrO^2 = Cr^2O^3.CrO^3 = \left.\begin{matrix}Cr^{vi}\\(Cr^2)^{vi}\end{matrix}\right\}O^6$. This compound separates, according to A. Vogel (*J. pr. Chem.* lxxvii. 482; *Jahresb.* 1859, p. 171), from a solution of potassium dichromate, mixed with ammonia, or with alcohol, and exposed to sunshine. According to H. Schiff (*Ann. Ch. Pharm.* cxx. 207; *Jahresb.* 1861, p. 250), it is formed by the action of a solution of chloride of lime on chromic hydrate or violet chromic chloride. It may be quickly and easily prepared by stirring up an intimate mixture of equal parts of potassium dichromate and crystallised oxalic acid with strong nitric acid to a thick paste, heating this paste in a porcelain crucible to a temperature below the melting point of the resulting potassium nitrate as long as red vapours are given off, then pulverising the porous easily separating mass, and digesting it with cold water. The aqueous solution thereby obtained yields, on addition of ammonia, a further quantity of the brown oxide. This oxide is resolved by prolonged washing with water, into chromic acid and chromic oxide, whence it appears to consist of chromic chromate rather than of the dioxide. The same view is supported by the fact that it does not turn guaiacum tincture blue, a property exhibited by all true peroxides. The same view of its composition is taken by Elliot a. Storer (*Rép. Chim. app.* iii. 390; *Jahresb.* 1861, p. 251), who also find that it gives up chromic acid to water and to solution of sal-ammoniac. They obtained a brown oxide having the constant composition $Cr^2O^3.CrO^3$ by Vogel's method above described, and by that of Krüger (*Gmelin's Handbook*, iv. 114), which consists in oxidising chromic oxide at 200°–210° in contact with the air. On the other hand, the brown oxides obtained by precipitating chrome-alum with neutral potassium chromate (5 eq. of the latter are required to produce a permanent precipitate), by treating chromic oxide with chlorine-water, and by heating chromium trioxide to 200°, as recommended by Traube (*Jahresb.* 1847–48, p. 415), proved to be mixtures of variable composition. Elliot a. Storer have endeavoured to replace the base in the compound $Cr^2O^3.CrO^3$ by an analogous sesquioxide. By adding 5 mol. neutral potassium chromate to a solution of 1 mol. common alum, a precipitate is formed consisting of *aluminium chromate*, $Al^2O^3.CrO^3$; the *ferric compound* formed in like manner contains $Fe^2O^3.CrO^3$, and an analogous compound containing both manganic and chromic oxides has been obtained by Fairrie (i. 935). Chromic chromate is also formed by passing the vapour of chromyl dichloride, mixed with hydrogen gas, through a red-hot glass tube (Schafarik, *Jahresb.* 1863, p. 225); and finally by boiling the solution of an acid chromate or of potassio-ammonium chromate with sodium hyposulphite (E. Kopp, *ibid.* 1864, p. 233).

Chromium Oxychlorides. 1. *Chromyl dichloride*, $(CrO^2)''Cl^2$ or  $Cl-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{Cr}}-Cl$, commonly called *Chlorochromic acid.*—According to Thorpe (*Chem. Soc. J.* [2] vi. 514), this compound boils at 116·8° under a pressure of 733 mm., a determination which agrees with that of Walter (i. 954), viz. 118° under a pressure of 760 mm. Its sp. gr. at 25° is 1·920 (Walter found 1·71 at 21°). Its specific volume calculated therefrom agrees with that of the analogously constituted sulphuryl chloride:

	Mol. weight	Sp. gr.	Sp. volume
SO^2Cl^2 . . .	135·0	1·66	81·8
CrO^2Cl^2 . . .	155·5	1·92	81·2

The vapour of chromyl dichloride imparts to the non-luminous flame of a Bunsen's burner a peculiar pale violet colour, and the spectrum exhibits three violet, eight green, one yellow, three orange, and two red lines, the brightest of which are the violet, and one of those situated in the green. When the flame is fed with a mixture of the vapour and oxygen gas, a spectrum of almost insupportable brightness is produced, the violet lines appearing peculiarly distinct. Neither chlorine gas nor chromic chloride nor chromous chloride introduced into the flame produces any similar spectrum. The deep red vapours of chromyl dichloride interposed before the slit of the spectral apparatus absorb all the light, excepting a narrow band of the red (Gottschalk a. Drechsel, *Bull. Soc. Chim.* [2] vi. 20).

2. *Chromium Chromato-chloride.* $Cr^3Cl^2O^6$ (Thorpe, *Chem. Soc. J.* [2] viii. 31).—Chromyl dichloride heated to 180°–190° in a sealed tube for three or four hours is almost wholly resolved into this compound and free chlorine:

$$3CrO^2Cl^2 = Cr^3Cl^2O^6 + 2Cl^2.$$

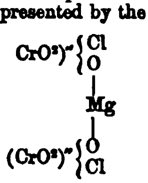
On opening the tube, the free chlorine escapes, and chromium chromato-chloride remains, mixed with unaltered chromyl dichloride, the greater part of which may be expelled by a gentle heat, and the rest by heating the substance to 120° in a current of carbon dioxide.

Chromium chromato-chloride is a black uncrystalline powder, which deliquesces rapidly in the air to a dark reddish-brown syrupy liquid smelling of free chlorine. It dissolves quickly in water, forming a dark brown solution which likewise evolves chlorine on standing. In strong hydrochloric acid it also dissolves with dark brown colour, and the solution when boiled gives off chlorine, becomes greenish-yellow, and ultimately exhibits the dark green colour peculiar to a solution of chromic oxide in hydrochloric acid. When the black compound is thrown into dilute ammonia, chromic acid is dissolved, together with all the chlorine, and a precipitate is formed consisting of chromium dioxide or chromic chromate, $Cr^2O^3.CrO^3$. When gently heated in hydrogen, it takes fire, the combustion proceeding rapidly through the mass, and is ultimately converted into chromic oxide, hydrochloric acid, and water:

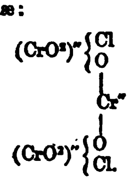
$$2Cr^3Cl^2O^6 + 10H = 3Cr^2O^3 + 4HCl + 3H^2O.$$

Chromium chromato-chloride is analogous in composition to the compounds $KCl.CrO^3$ and $MgCl^2.2CrO^3$, obtained by Peligot (*Ann. Ch. Phys.* [2] lii. 267), and might be represented in like manner by the formula $Cr''Cl^2.2CrO^3$. But its reaction with hydrogen shows that the chlorine is not present in the form of chromous chloride, for that compound may be heated to fusion in hydrogen without forming hydrochloric acid.

The black chromium-compound and the corresponding magnesium-compound may perhaps be better represented by the following formulæ:



$$\begin{array}{l}CrO^2)''\left\{\begin{matrix}Cl\\O\end{matrix}\right.\\ \qquad\quad |\\ \qquad\quad Mg\\ \qquad\quad |\\ (CrO^2)''\left\{\begin{matrix}O\\Cl\end{matrix}\right.\end{array}$$



$$\begin{array}{l}(CrO^2)''\left\{\begin{matrix}Cl\\O\end{matrix}\right.\\ \qquad\quad |\\ \qquad\quad Cr''\\ \qquad\quad |\\ (CrO^2)''\left\{\begin{matrix}O\\Cl\end{matrix}\right.\end{array}$$

The *hydroxychlorides* $Cr(HO)^2Cl^4$ and $Cr(HO)^4Cl^2$ obtained by Schiff have been already mentioned (p. 451).

Chromic Sulphides. The sulphide obtained by fusing potassium chromate with liver of sulphur forms greenish-black friable crystals, of sp. gr. 2·79, is easily oxidised by nitric acid, and when ignited in the air burns with a glimmering light to chromic oxide having an alkaline reaction; but the sulphide produced by igniting chromic chloride in hydrogen sulphide forms grey-black, metallic, shining, flexible laminæ, of sp. gr. 3·77; is not attacked by fuming nitric acid; and when ignited is converted, without alteration of form, into the green sesquioxide. The first-mentioned product is probably an alkaline double sulphide (Schafarik, *Jahresb.* 1863, p. 225).

CHRYSAMMIC ACID. $C^7H^2N^2O^6$.*—The following method of preparing this acid is given by Stenhouse a. Müller (*Chem. Soc. J.* [2] iv. 319): 2 pts. of Socotrine aloes are added to 6 pts. of nitric acid of sp. gr. 1·36, heated nearly to boiling in a retort provided with a condensing arrangement, and the mixture is heated for about ten hours—the first portions of acid which pass over being poured back—till it is reduced to about half its original volume; 3 pts. more of nitric acid are then added; the digestion is continued for 6 or 7 hours longer; the greater portion of the nitric acid then distilled off; the residue mixed with 4 pts. water; and the mixture of picric and aloetic acids which remains undissolved is digested for six or eight hours with an equal weight of nitric acid of sp. gr. 1·45, and then washed by decantation with boiling water, till the wash-water, which is at first orange-yellow, exhibits a purple-red colour. The mixture of chrysammic and aloetic acid thus freed from picric acid is dried, again digested for about ten hours, with an equal weight of strong nitric acid; and the product, after washing with hot water, is repeatedly boiled with four times its weight of water till the filtrate is no longer purple-red, but light-red. After renewed boiling with water and a slight excess of chalk, the liquid becomes dark red or purple-red, and on cooling deposits calcium chrysammate, partly in needles, partly as a flocculent mass, which must be recrystallised from weak spirit. If much aloetic acid is still present, in consequence of imperfect transformation of the aloes, the calcium chrysammate crystallises only after repeated boiling with water, and cooling, whereby the more soluble aloetate is removed. The red wash-waters obtained in this process yield, when acidulated with nitric acid, a large quantity of impure aloetic acid, which by further treatment with strong nitric acid may be converted into chrysammic acid. Aloes thus treated yields from 3 to 4 p. c. calcium chrysammate: it is more economical however to make use of the otherwise worthless resinous portion of the aloes, which is insoluble in cold water, though the quantity of chrysammic acid obtained therefrom is not more than half of that yielded by the aloes itself. Chrysammic acid is also produced, as shown by De la Rue a. Müller (*Jahresb.* 1862, p. 324), by the action of nitric acid on chrysophane and other constituents of rhubarb.

Chrysammic acid separated by nitric acid from the hot solution of the calcium salt forms large scales like lead iodide, quite insoluble in cold water. The acid suspended in water decomposes the neutral solutions of cupric acetate and nitrate, nickel sulphate, manganous chloride, and other salts. Treated with *potassium chlorate* and *hydrochloric acid*, it is slowly converted into chloropicrin, without formation of chloranil. Heated with *benzoyl chloride*, it yields nearly insoluble benzoyl-chrysammic acid, $C^7H(C^7H^5O)N^2O^6$, which crystallises in prisms and is decomposed only by alcoholic potash into benzoic and chrysammic acids (Stenhouse a. Müller). By *potassium cyanide* in aqueous solution it is converted into chrysocyamic acid (Finckh, *Ann. Ch. Pharm.* cxxxiv. 229):

$$\underset{\substack{\text{Chrysammic}\\ \text{acid.}}}{C^7H^2N^2O^6} + 3CNH + 2H^2O = \underset{\substack{\text{Chrysocyamic}\\ \text{acid.}}}{C^9H^3N^3O^6} + 2NH^3 + CO^2.$$

Calcium Chrysammate, $(C^7HN^2O^6)^2Ca$ (at 145°), is easily soluble in boiling alcohol, less soluble in water, and crystallises from the latter in light red needles, which when dried in a vacuum give off water and turn brown. The *magnesium salt* $(C^7HN^2O^6)^2Mg$ (at 160°) crystallises in broad red tables. The *cupric salt* is prismatic and more soluble than the calcium salt. The *manganous salt* crystallises in scales having a blood-red colour by transmitted light, and a golden lustre; like most chrysammates, it is moderately soluble in weak spirit (Stenhouse a. Müller).

Ethyl Chrysammate, $C^7HN^2O^6.C^2H^5$, is obtained by heating dry silver chrysammate to 100° with 5 pts. ethyl iodide. When purified by repeated crystallisation from benzol, and finally from ether, it forms pale red needles or yellow prisms nearly insoluble in carbon bisulphide, and only slightly soluble in ether (Stenhouse, *Chem. Soc. J.* [2] iv. 324).

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* Graebe a. Liebermann (*Zeitschr. f. Chem.* [2] iv. 503) regard chrysammic acid as *tetranitro-dioxy-anthraquinone*, $C^{14}H^4N^4O^{12} = C^{14}H^2(NO^2)^4(HO)^2O^2$.

Hydrochrysammide, $C^7H^6N^2O^3$ (iii. 191), is easily formed by treating chrysammic acid with zinc and dilute acid, or with hydriodic acid (with addition of a little phosphorus), or with sodium-amalgam. The purple-red solution produced in the latter case becomes orange-coloured when shaken up with the amalgam in closed vessels, but recovers its original colour on exposure to the air (Stenhouse a. Müller, *loc. cit.*).

CHRYSANILINE. $C^{20}H^{17}N^3$ (iv. 473).—This base forms two picrates, of which the *dipicrate* $C^{20}H^{17}N^3[C^6H^2(NO^2)^3O]^2$ is the less soluble. It is obtained by precipitating a chrysaniline salt with an aqueous solution of picric acid, washing the precipitate, and dissolving it in alcohol. On mixing a cold-saturated solution of a chrysaniline salt with a cold-saturated solution of picric acid in alcohol, the dipicrate gradually separates in splendid ruby-coloured needles which retain 1 mol. water at 100°, but become anhydrous at 110° (Hofmann, *Deutsch. chem. Gesells.* Berlin, 1869, p. 379).

Trimethyl-chrysaniline. $C^{20}H^{14}(CH^3)^3N^3$.—The di-hydriodide of this base is obtained by heating 1 mol. chrysaniline with 4 mol. methyl-iodide to 100° for five or six hours, in shining needles which may be purified by washing with boiling alcohol, and recrystallisation from boiling water. It then separates in splendid needles having a colour intermediate between orange-yellow and carmine-red, and consisting when dried at 100° of $C^{20}H^{14}(CH^3)^3N^3.2HI$. The solution of this salt dyes silk and wool deep orange-yellow, with a tinge of scarlet. The hot-saturated aqueous solution of this salt mixed with excess of ammonia becomes light yellow, and deposits on cooling interlaced yellow needles of the *monohydriodide* $C^{20}H^{14}(CH^3)^3N^3.HI$. The mother-liquors obtained in determining the iodine in these two salts, freed from silver by hydrochloric acid and mixed with platinic chloride, yielded the *platinum salt* $C^{20}H^{14}(CH^3)^3N^3.2HCl.PtCl^4$ in beautiful interlaced needles. The solution of either of the hydriodides warmed with silver-oxide yields the *base*, as a brown-yellow uncrystallisable powder, insoluble in water, soluble in alcohol. With acids it forms well-crystallised salts, most of which are very soluble; the nitrate and picrate however are sparingly soluble.

Triethyl-chrysaniline.—The dihydriodide $C^{20}H^{14}(C^2H^5)^3N^3.2HI$ is prepared like the corresponding methyl-compound, which it resembles in every respect. When dried under the air-pump, it retains 1½ mol. water, which it gives off at 100°. The *platinochloride* $C^{20}H^{14}(C^2H^5)^3N^3.2HCl.PtCl^4$ crystallises in needles slightly soluble in water.

The hydriodide of *triamyl-chrysaniline* has also been obtained in the crystalline form.

When chrysaniline is heated to the boiling point with excess of aniline and acetic acid, ammonia is given off and a dark brown solution is formed from which, after addition of alkali, the free aniline may be removed by a current of steam. From the brown residue, a dark brown hydrochloride of a phenylated chrysaniline may be prepared, which crystallises in four-sided tables (Hofmann, *Deutsch. chem. Gesells.* Berlin, 1869, p. 377; *Zeitschr. f. Chem.* [2] v. 634).

CHRYSANISIC ACID. Kellner a. Beilstein (*Ann. Ch. Pharm.* cxxviii. 179) represent this acid by the formula $C^7H^4(NO^2)^3$, according to which it is isomeric with trinitrotoluene. Cahours, by whom it was discovered, assigned to it the formula $C^7H^5(NO^2)^3O$, making it isomeric with trinitrocresol. The *ammonium salt* $C^7H^4(NO^2)^3.NH^4$ is easily soluble in water, and crystallises in light brown needles; the *silver salt* $C^7H^4(NO^2)^3Ag$ is a bulky yellow precipitate. The *ethylic ether* $C^7H^4(NO^2)^3.C^2H^5$, produced by treating the alcoholic solution of the acid with hydrochloric acid gas, crystallises from alcohol in large laminæ having a golden lustre, and remaining suspended in the liquid, with a sky-blue iridescence.

Amidochrysanisic acid, $C^7H^7N^3O^4 = C^7H^3(NH^2)(NO^2)^2$, produced by the action of hydrogen sulphide on an alcoholic solution of chrysanisic acid supersaturated with ammonia, crystallises in red microscopic crystals, easily soluble in alcohol, sparingly soluble in hot water, insoluble in ether. Its *ammonium salt*, $C^7H^6N^3O^4.NH^4$, forms garnet-red monoclinic prisms with dihedral summits, having the axes $a : b : c = 1{\cdot}0730 : 1 : 1{\cdot}809$, and the angle $b : c = 77° 32'$. The potassium salt and the barium salt crystallise in red needles; the salts of the heavy metals produce in the solution of ammonium amidochrysanisate, orange-coloured or yellow precipitates.

Azo-amidochrysanisic acid, $C^7H^2N(NH^2)(NO^4)^2$, separates on passing nitrous acid into the alcoholic solution of amidochrysanisic acid, as a brass-yellow crystalline body, easily soluble in absolute alcohol and not decomposed by boiling with acids. It dissolves in ammonia, with evolution of nitrogen, forming a red liquid, from which acids throw down a body which crystallises from hot water in yellow laminæ and has the composition $C^{14}H^{10}N^2(NO^2)^4O$ (Kellner a. Beilstein).

CHRYSENE. $C^{18}H^{12}$.—This hydrocarbon, discovered by Laurent (i. 958), occurs, together with benzerythrene (p. 304), in the least volatile portion of crude anthracene (the mixture of solid hydrocarbons which remains in the distillation of coal-tar after the naphthalene has passed over). It is contained also in larger quantity in the reddish-yellow product which passes over last in the destructive distillation of dry fir-wood tar (*brai sec*) (Berthelot, *Jahresb.* 1867, p. 605). It is formed, together with diphenyl and many other hydrocarbons, when the vapour of benzene is passed through a porcelain tube heated to bright redness (p. 261). The formation of diphenyl and chrysene may be represented by the equations,

$$\underset{\text{Benzene.}}{2C^6H^6} = \underset{\text{Diphenyl.}}{C^{12}H^{10}} + H^2; \qquad 2C^{12}H^{10} = \underset{\substack{\text{Intermediate}\\ \text{product.}}}{C^{24}H^{18}} + H^2;$$

$$C^{24}H^{18} = \underset{\text{Chrysene.}}{C^{18}H^{12}} + \underset{\text{Benzene.}}{C^6H^6}$$

Chrysene is also formed, together with benzene (probably from phenylene as intermediate product), when diphenyl is heated for an hour with hydrogen in a sealed tube (Berthelot, *ibid.* pp. 542, 544):

$$3C^{12}H^{10} = 3C^6H^6 + C^{18}H^{12}.$$

A mixture of chrysene vapour and hydrogen gas passed through a red-hot tube is converted into benzene and diphenyl:

$$C^{18}H^{12} + 2H^2 = C^6H^6 + C^{12}H^{10};$$

and a mixture of chrysene and ethylene similarly treated yields benzene and anthracene, with a small quantity of naphthalene (Berthelot, *ibid.* p. 546):

$$C^{18}H^{12} + C^2H^4 = C^6H^6 + C^{14}H^{10}$$

and

$$C^{18}H^{12} + 2C^2H^4 = 2C^6H^6 + C^{10}H^8.$$

Chrysene added to a hot alcoholic solution of picric acid (saturated at 20°-30°) forms a yellow granular precipitate of *chrysene picrate*, consisting of scaly groups of microscopic needles. If benzerythrene is also present, the scales are changed into brown spherical aggregates of needles (Berthelot, *ibid.* 1867, p. 604). According to Gellatly (*Chem. News*, x. 243), chrysene picrate, $C^{18}H^{12}.C^6H^3(NO^2)^3O$, crystallises from a hot solution of its components in Boghead naphtha, in reddish-brown needles often half an inch long.

CHRYSINIC ACID. A yellow colouring matter contained in the buds of *Populus nigra* and *P. pyramidalis*. (See POPLAR-BUDS, v. 688.)

CHRYSOCYAMIC ACID. $C^9H^5N^3O^6$ (C. Finck, *Ann. Ch. Pharm.* cxxxiv. 229).—An acid allied to isopurpuric acid, produced by heating chrysammic acid with aqueous potassium cyanide:

$$C^7H^2N^2O^6 + 3CNH + 2H^2O = C^9H^5N^3O^6 + 2NH^3 + CO^2.$$

The *potassium salt* resulting from the reaction, after being purified by repeated precipitation with potassium carbonate, and finally by recrystallisation from hot water, separates on cooling as a dark-coloured salt containing $2C^9H^4N^3O^6K.3H^2O$, and giving up its water at 120°. The *ammonium salt* $2C^9H^4N^3O^6.NH^4.3H^2O$ forms dark green needles less soluble in water than the potassium salt. The *barium salt* $(C^9H^4N^3O^6)^2Ba$, the *calcium salt* $(C^9H^4N^3O^6)^2Ca$, the *lead salt* $(C^9H^4N^3O^6)^2Pb$, and the *silver salt* $C^9H^4N^3O^6Ag$, are red-brown precipitates which acquire metallic lustre by trituration, and detonate when heated. The *acid* $2C^9H^5N^3O^6.3H^2O$ separated from the potassium salt by nitric acid, is insoluble in water, soluble in alcohol, and exhibits metallic lustre when dry.

CHRYSOGEN (Fritzsche, *Compt. rend.* liv. 910; further, *Bull. Soc. Chim.* [2] vi. 474).—An orange-coloured hydrocarbon contained in small quantity in crude anthracene, separable therefrom by repeated crystallisation from light coal-tar naphtha, and finally purified by treatment with alcohol and ether. It dissolves in 2,500 pts. of cold benzol, and in 500 pts. at the boiling heat; very sparingly also in alcohol and ether; and separates from the hot-saturated solutions in groups of orange-coloured tables or laminæ, which appear gold-green in the liquid by reflected light, and are converted by ether into an orange-coloured powder. It contains 94·3 to 95·0 p. c. carbon and 5·7 to 4·7 p. c. hydrogen; melts at 280° to 290°; sublimes with partial decomposition; dissolves without alteration in strong sulphuric acid; and yields a crystalline product with strong nitric acid. When mixed, even in traces, with colourless hydrocarbons, it imparts to them a fine yellow colour. Its solution when exposed to sunshine quickly becomes colourless, and then yields a crystallisable colourless body, which becomes orange-yellow when fused.

CHRYSOPHANE. $C^{16}H^{18}O^{8}$.—An orange-red bitter substance contained, according to Kubly (*Bull. Soc. Chim.* [2] x. 293), in the alcoholic extract of rhubarb, and resolvable by acids into chrysophanic acid and sugar.

CHRYSOPHANIC ACID. H. Grothe (*Pogg. Ann.* cxiii. 190) has obtained this acid from the root of *Rheum pyramidale*, also of *Rumex Patientia*, *R. palustris*, *R. acutus*, *R. aquaticus*, and *R. Hydrolapathum*, and regards it as nearly allied to the yellow colouring matter of buckwheat. J. B. Batka (*Chem. Centr.* 1864, p. 622) prepares it by treating rhubarb or the leaves or petals of senna with caustic potash, precipitating the filtrate, and dissolving the washed and dried precipitate in chloroform, which on evaporation leaves the acid in granular crystals of a pure yellow colour. The substances obtained from rhubarb-root, and known in commerce as phæoretin and erythroretin, are, according to Batka, nothing but impure chrysophanic acid, the former in a half-charred condition, the latter contaminated with rheitannic acid.

The composition of chrysophanic acid has been represented by the formulæ $C^{10}H^{8}O^{3}$ and $C^{14}H^{10}O^{4}$[*] (i. 959). According to Rochleder (*Zeitschr. f. Chem.* [2] v. 576), chrysophanic acid prepared from rhubarb usually contains emodin. On boiling it with soda-ley and filtering at the boiling heat, the emodin dissolves, with blood-red colour, whilst nearly all the chrysophanic acid remains undissolved, and when further purified by crystallisation from alcohol of 90 p. c. gives by analysis numbers agreeing with the formula $C^{14}H^{10}O^{4}$. According to Graebe a. Liebermann (*ibid.* iv. 503), chrysophanic acid is isomeric with alizarin, $C^{14}H^{8}O^{4}$, and when treated with zinc-dust is converted into anthracene (p. 177).

A solution of chrysophanic acid in *benzoyl chloride* heated nearly to the boiling point of the latter, gives off hydrochloric acid and yields dibenzoyl-chrysophanic acid, $C^{10}H^{6}(C^{7}H^{5}O)^{2}O^{3}$ or $C^{14}H^{8}(C^{7}H^{5}O)^{2}O^{4}$, [$C^{14}H^{6}(C^{7}H^{5}O)^{2}O^{4}$ according to Graebe a. Liebermann], as a fibro-crystalline mass, which dissolves sparingly in alcohol, and crystallises from benzol, or, better, from a mixture of benzol and absolute alcohol or amylic alcohol, in long irregularly hexagonal prisms. It melts at 200°, gives off at higher temperatures, yellow vapours smelling like bitter almond oil, and is not decomposed by ammonia; with potash-ley of sp. gr. 1·5 it gives the characteristic red colour only after long boiling; by alcoholic potash or strong sulphuric acid it is immediately resolved into benzoic and chrysophanic acids. With *acetyl chloride* chrysophanic acid yields acetyl-chrysophanic acid, which is crystallisable, but difficult to purify. Gently heated with *phosphorus pentachloride* it yields a body which reacts like chrysophanyl chloride, being converted into chrysophanic acid by boiling with water. A solution of chrysophanic acid in *fuming nitric acid* deposits after a few days large laminar crystals of chrysammic acid (p. 457) identical in every respect with that obtained from aloes (De la Rue a. Müller, *Jahresb.* 1862, p. 323).

CHRYSOPICRIN. Syn. with VULPIC ACID (v. 1007).

CHRYSOTOLUIDINE. $C^{21}H^{21}N^{3}$.—A yellow base related to toluidine in the same manner as rosaniline to a mixture of 2 mol. toluidine and 1 mol. aniline. It is found, together with other bases, among the secondary products formed in the industrial preparation of rosaniline (p. 165), being produced by the action of dehydrogenising agents on toluidine, 3 mol. of that base giving up 3 mol. hydrogen:

$$\underset{\text{Toluidine.}}{3(C^{7}H^{7}.H^{2}.N)} = \underset{\text{Chrysotoluidine.}}{C^{21}H^{21}N^{3}} + 3H^{2}.$$

By the exchange of 3 at. hydrogen for 3 at. tolyl, phenyl, or ethyl, it is capable of yielding new colouring matters: *e.g.*,

$$\underset{\text{Chrysotoluidine.}}{C^{21}H^{21}N^{3}} + 3(C^{7}H^{7}.H^{2}.N) = \underset{\substack{\text{New colouring}\\\text{matter.}}}{C^{21}H^{18}(C^{7}H^{7})^{3}N^{3}} + 3NH^{3}.$$

(De Laire, Girard a. Chapoteaut, *Compt. rend.* lxiii. 964.)

CHURCHITE. A hydrated calcio-cerous phosphate from Cornwall, occurring on a quartz-rock as an incrustation resembling wavellite, consisting of fan-shaped groups of small prisms, apparently monoclinic. Colour, pale smoke-grey, with a tinge of flesh-red; hardness, rather more than 3; sp. gr. (approximate) = 3·14. Analysis gave 51·87 p. c. CeO, 5·42 CaO, 28·48 P^2O^5, and 14·93 water containing a little hydrofluoric acid, whence the formula:

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[*] In the first edition the formula is erroneously printed $C^{17}H^{10}O^{6}$.

$$5CeO.CaO.2P^2O^5.8H^2O \text{ or } (\tfrac{5}{6}Ce\tfrac{1}{6}Ca)^3P^2O^8.8H^2O$$

(Church, *Chem. Soc. J.* [2] iii. 259). C. Greville Williams (*Chem. News*, xii. 183) has found by optical examination that the mineral also contains didymium.

CINCHONA-BARK. When a bark containing quinine or cinchonine is heated in a test-tube, a characteristic red vapour is given off, which condenses to an oily liquid having a splendid carmine-red colour. This reaction is not exhibited by false cinchona-barks, or by the true barks after the alkaloïds have been removed from them by acids (Grahe, *Chem. Centr.* 1858, p. 97; see also Batka, *ibid.* 1859, p. 865).

Quantitative Estimation of the Alkaloïds.—1. Claus (*Russ. Zeitschr. Pharm.* i. 585; *Jahresb.* 1863, p. 707) exhausts the bark, dried at 100°, with cold dilute sulphuric acid; evaporates the extract with excess of magnesia; dissolves out the quinine from the residue with ether, and the other bases with alcohol.—2. De Vrij (*Pharm. J. Trans.* [2] vi. 50) mixes the pulverised bark, dried at 100°, with one-fourth of its weight of slaked lime; boils the mixture for about five minutes with 10 pts. alcohol of sp. gr. 0·85; and then exhausts it on a filter with a large quantity of boiling alcohol. The alcoholic solution acidulated with acetic acid is next evaporated, and the residue repeatedly treated with water, as long as the filtrate becomes turbid on addition of alkali. The bases are thereby dissolved, whilst quinonic acid, fats, and resinous substances remain on the filter. The bases are then precipitated from the concentrated aqueous solution by milk of lime; and the precipitate is washed with a little water, and then exhausted at the boiling heat with alcohol of sp. gr. 1·82. The alcoholic solution, when evaporated, yields the whole of the bases, sometimes contaminated with a small quantity of resinous matter insoluble in acetic acid. The bases are redissolved in acetic acid, and the solution is agitated in a closed tap-funnel with a slight excess of caustic soda and with ether (at least 15 pts.), and the ethereal solution is separated after standing for six hours. This solution when evaporated leaves the whole of the quinine, together with traces of cinchonidine, quinidine, and cinchonine, and frequently of a fusible base. The bases insoluble in ether are redissolved in dilute acetic acid. If quinidine is present, the resulting solution, mixed with a few drops of concentrated aqueous potassium iodide, yields a sandy precipitate of quinidine hydriodide, $C^{20}H^{24}N^2O^2.HI$, which must be weighed after drying at 100°. The filtrate yields with caustic soda a precipitate consisting of cinchonine, or of a mixture of cinchonine and cinchonidine. The presence of the latter can be determined with certainty only by its behaviour to polarised light (i. 971).

3. According to Van der Burg (*Zeitschr. anal. Chem.* iv. 273; *Jahresb.* 1865, p. 736), the extraction of the bases of cinchona-bark by lime and alcohol is not complete unless the treatment be repeated several times at the boiling heat; moreover, a certain quantity of the lime is always dissolved, increasing the total weight of the alkaloïds obtained, and being ultimately reckoned as cinchonine. For the estimation of the total quantity of the bases, Van der Burg recommends the following method: The bark is exhausted by repeated boiling with alcohol, with addition of calcium hydrate; the solution is mixed with acetic acid and evaporated; and the filtered aqueous solution of the residue is precipitated with caustic soda. The precipitate is freed from colouring matter, in the manner recommended by Rabourdin (*Jahresb.* 1861, p. 533), viz. by solution in hydrochloric acid and fractional precipitation with ammonia; the pure precipitate is finally dissolved in alcohol, the solution evaporated in a platinum capsule, and the residue weighed. This gives the total amount of organic bases in the bark. As quinine and quinidine are perceptibly soluble in pure water, it is advisable, after precipitating with soda-ley and washing the precipitate, to collect the wash-water separately as soon as it ceases to exhibit alkaline reaction, agitate it with ether, and add the residue obtained by evaporating the ethereal solution to the quantity of the bases obtained by precipitation.

4. For the estimation of quinine in cinchona-barks, the following volumetric method is given by Glénard a. Guillermond (*Compt. rend.* xlvii. 831; *J. Pharm.* [3] xxxvii. 5): The finely pulverised bark (10 grms.), intimately mixed with an equal weight of slaked lime, is exhausted in a well-closed vessel with a determinate quantity (100 c.c.) of ether free from water and alcohol, and a portion (10 c.c.) of the ethereal solution is agitated with a known and excessive volume of titrated sulphuric acid [10 c.c. of which contain 0·0302 grms. H^2SO^4, equivalent to 0·2 grms. quinine, on the supposition that the salt produced by saturation has the composition $(C^{20}H^{24}N^2O^2)^2.H^2SO^4$];

and the unsaturated acid is determined by titration with ammonia; the quantity of quinine which saturates the rest of the acid may then be calculated. To determine the point of saturation, Glénard a. Guillermond use, instead of litmus, an ethereal solution of the colouring matter of Campeachy wood. In a subsequent memoir (*J. Pharm.* [3] xli. 40), the same authors recommend, instead of normal sulphuric acid, an aqueous solution of oxalic acid (4·0806 grm. of the air-dried crystallised acid in a litre), and replace the aqueous ammonia by an aqueous (not alcoholic) solution of pure potassium or sodium hydrate; for determining the point of saturation they use an alcoholic extract of St. Martha wood, which, in contact with free alkali, immediately assumes a bright red colour.

From the investigations of De Vrij (*Pharm. J. Trans.* [2] v. 593; vi. 15), it appears that the root-bark of various species of cinchona cultivated on the Neilgherry mountains in British India is richer in organic bases than the stem-bark, and that the amount of these bases in the bark may be increased by careful management, inasmuch as the bark of a young stem of *C. succirubra* scarcely two years old, which had been covered with moss to accelerate the thickening of the bark, was found to contain 8·409 p. c. of cinchona-bases. In the leaves of *C. succirubra* growing at a height of 1,600 feet above the sea-level, De Vrij found 2·06 p. c. quinovic acid; the same species at the height of 5,200 feet was found to contain only 1·3 p. c. quinovic acid. Respecting the proportions of quinovin or quinovin-bitter in various parts of cinchona-trees, see Quinovin (v. 32).

The bark of *Cinchona macrocalyx*, Pav., known in commerce as 'China de Cuença,' contains, according to J. K. Fischer (*Zeitschr. f. Chem.* [2] ii. 256), 2·38 p. c. organic bases, of which 0·59 p. c. consists of quinine and 1·79 p. c. of cinchonine.

De Vrij regards it as probable that cinchona-barks originally contain an amorphous base which yields amorphous salts, inasmuch as he obtained such a base from barks grown in Java, which had been dried and exhausted with acetic acid in the dark (*Jahresb.* 1866, p. 471).

Howard (*Pharm. J. Trans.* [2] vi. 584) has described and delineated the crystallised constituents of cinchona-bark (*C. succirubra*).

Respecting a brown humus-like substance obtained from certain cinchona-barks, see Lignoïn (iii. 695).

Cinchona Cultivation in India.—The cultivation of cinchona-trees has within the last ten years been carried on with great success in British India. The chief seat of the cultivation is Ootacamund, in the Neilgherries, from which it extends nearly to the southern point of Hindostan, in some places at heights of 7,000 to 8,000 feet above the sea-level. The cinchonas were first introduced at Ootacamund in 1860; in 1862 there were upwards of 72,000 plants under cultivation, more than half of which consisted of *C. succirubra*, and 1,000 of *C. Calisaya*, both valuable species. In May 1866 the numbers of different species growing at Ootacamund were as follows:

Cinchona succirubra	297,000
„ Calisaya	37,000
„ officinalis	758,000
Species yielding grey barks	29,000
C. lancifolia and C. pitayensis	198
C. Pahudiana	425

Altogether, including a few other species occurring in small numbers, 1,123,000 plants.

The cultivation was also introduced at Hakgalla in the central mountain-land of Ceylon in 1861, and at Darjeeling in the south-eastern Himalaya in 1862. Hakgalla in 1863 possessed 22,000 cinchona-trees, and in November 1865 more than 500,000, principally *C. succirubra* and *C. officinalis*. Darjeeling and Rungbee in Sikkim possessed in May 1866 more than 300,000 plants, chiefly of the same two species. From these plantations young cinchona-trees have been transplanted to other parts of India, as the Punjaub, Assam, Rangoon, and Bengal, also to the islands of Mauritius and Réunion, and to Australia, New Zealand, Jamaica, and other localities where the climate and soil appear to be adapted to their cultivation (Flückiger's *Pharmakognosie des Pflanzenreiches*, Berlin, 1867, p. 422).

CINCHONA-RED (i. 969) is formed, together with sugar, by boiling quinotannic acid with dilute sulphuric acid. When dissolved in ammonia, precipitated by hydrochloric acid, and dried at 130°, it has the composition $C^{28}H^{22}O^{14}$. Its barium-compound precipitated from the ammoniacal solution contains $C^{28}H^{20}O^{14}Ba$; the calcium-compound $C^{28}H^{20}O^{14}Ca$. Fused with potash, it yields a brown humous product, chiefly protocatechuic acid, together with a little acetic acid. The liquid separated from the cinchona-red contains glucose (Rembold, *Ann. Ch. Pharm.* cxliii. 270).

CINCHONIDINE. $C^{20}H^{24}N^2O$.—This base and its salts have been examined by Hesse (*Ann. Ch. Pharm.* 325), with results differing in many respects from those given in vol. i. p. 971. The pure base is obtained by mixing the preparation containing quinine-salt with sodio-potassic tartrate, dissolving the resulting precipitate in hydrochloric acid, and precipitating with ammonia. On treating the bases thereby separated with ether, the cinchonidine chiefly remains undissolved, and may be purified by recrystallisation of its neutral hydrochloride.

Cinchonidine crystallises in large anhydrous prisms soluble at 10° in 76·4 pts. ether, in 19·7 pts. of 80 p. c. alcohol (in 15·3 pts. at 20°), in 1680 pts. of cold and a somewhat smaller quantity of hot water. It melts at 206·5°, and resolidifies in the crystalline form at 190° (comp. i. 971).

Salts of Cinchonidine.—The *hydrochloride*, $C^{20}H^{24}N^2O.HCl$ + aq., crystallises in large monoclinic double pyramids, dissolving at 10° in 325 pts. ether and 30·5 pts. water (at 20° in 20·1 pts.). On boiling down the solution, the salt separates in yellowish drops, which solidify in the cold to a radio-crystalline mass. The *aurochloride*, $C^{20}H^{24}N^2O.HCl.AuCl^3$, is a pulverulent mass of a fine yellow colour, melting at about 100°. The *platinochloride*, $C^{20}H^{24}N^2O.2HCl.PtCl^4$, is a pale orange-yellow crystalline powder nearly insoluble in cold water. The *dihydriodide*, $C^{20}H^{24}N^2O.2HI$ + aq., forms lemon-yellow prisms. The *nitrate*, $C^{20}H^{24}N^2O.NHO^3$ + aq., crystallises in large prisms, melting and giving off water at about 100°, and dissolving in 70·5 pts. water at 10°. The *hypophosphite* is more soluble than the corresponding quinine salt. The *acetate*, $C^{20}H^{24}N^2O.C^2H^4O^2$ + aq., is easily soluble in water, and crystallises in nodular groups of needles. The *benzoate*, $C^{20}H^{24}N^2O.C^7H^6O^2$, forms short white prisms soluble in 340 pts. water at 10°.

Sulphates.—The neutral sulphate, $2C^{20}H^{24}N^2O.SH^2O^4$ + 6aq., forms white prisms, becoming anhydrous at 100°, insoluble in ether, but dissolving in 97·5 pts. water at 12°. The anhydrous salt is also crystallisable under certain circumstances, and exhibits the peculiarity of producing other anhydrous salts by double decomposition. The *acid salt*, $C^{20}H^{24}N^2O.SH^2O^4$ + 5aq., crystallises in long striated efflorescent prisms easily soluble in water and in alcohol. The *hyperacid salt*, $C^{20}H^{24}N^2O.2SH^2O^4$ + 2aq., separates from the solution of the preceding salt in dilute sulphuric acid, by evaporation over sulphuric acid, in short prisms insoluble in ether and dissolving but slowly in cold water. The *hyposulphite*, $C^{20}H^{24}N^2O.S^2H^2O^3$ + 2aq., forms thin prisms which dissolve at 10° in 221 pts. water, become anhydrous at 110°, but reabsorb their entire amount of water on exposure to the air. The *neutral oxalate*, $2C^{20}H^{24}N^2O.C^2H^2O^4$ + 6aq., crystallises in long asbestos-like prisms, soluble in 252 pts. of water at 10°; the anhydrous salt in white nodules. The *succinate* forms prisms soluble in 582·5 pts. water at 10°. The *neutral tartrate*, $2C^{20}H^{24}N^2O.C^4H^6O^6$ + 2aq., is a white crystalline precipitate perfectly insoluble in potassio-sodic tartrate, separating from hot water in prisms, requiring for solution 1265 pts. water at 10°. As neutral tartrate of cinchonine is soluble in 35·6 pts. water at 16°, cinchonine and cinchonidine may be easily separated from one another in the form of tartrates. *Cinchonidine-antimonious tartrate* is easily soluble in hot water and in alcohol, and crystallises in prisms. The *citrate* forms prisms which are converted by water into a basic salt. The *hydroferricyanide* is an egg-yellow precipitate composed of spherical crystalline aggregates, or of laminæ.

CINCHONINE. $C^{20}H^{24}N^2O$.—Hesse (*Ann. Ch. Pharm.* cxxii. 226) has shown that the base called β-cinchonine, obtained by Schwabe from commercial quinoïdine (i. 974), does not differ in any respect from ordinary cinchonine.

Cinchonine sublimes partially at 220° and melts at 240°–250° (Hesse); 1 pt. of it (dried at 100°) dissolves in 2118 pts. ether at 170° (Van der Burg, *Zeitschr. anal. Chem.* iv. 273). From a solution containing tartaric acid it is not precipitated by acid sodium carbonate at ordinary temperatures; but on heating the liquid, carbon dioxide escapes and cinchonine is precipitated. Some of the neutral salts, as the acetate and citrate, are decomposed, and yield a precipitate of the base, even when heated with water (Hesse). According to Schützenberger (*Compt. rend.* xlvi. 1065), cinchonine treated with zinc and sulphuric acid takes up H^2O and is converted into a new base, $C^{20}H^{26}N^2O^2$.

Salts of Cinchonine (Hesse, *Ann. Ch. Pharm.* cxxii. 226; cxxxv. 326).—The *hydriodide*, $C^{20}H^{24}N^2O.HI$ + aq., separates on adding potassium iodide to a solution of the hydrochloride, partly as a pale yellow oil which solidifies to a crystalline mass, partly in slender white crystals. The *hydrochloride*, $C^{20}H^{24}N^2O.HCl$ + 2aq., crystallises in the form described by Schwabe (for the so-called β-salt, i. 975). The crystals are permanent in the air, effloresce over sulphuric acid, give off their water at 100°, and melt at 130°. Sp. gr. of the powder = 1·234. One part of the salt dissolves at 10° in 24 pts. water; at 16° in 1·3 pts. alcohol and 273 pts. ether. The *stannosochloride*, $C^{20}H^{24}N^2O.2HCl.SnCl^2$, separates in heavy yellow prisms from a mixture of the hydrochloride with acidulated stannous chloride. The *zincochloride*, $C^{20}H^{24}N^2O.2HCl.ZnCl^2 + aq.$, separates in flattened prisms from an alcoholic solution of cinchonine mixed with zinc chloride, and then with sufficient hydrochloric acid to redissolve the precipitate. A solution of this salt in excess of hydrochloric acid deposits the easily soluble salt $2(C^{20}H^{24}N^2O.3HCl)ZnCl^2 + 3aq.$ The *aurochloride*, $C^{20}H^{24}N^2O.2HCl.AuCl^3$, is a heavy light-yellow powder, melting at a little above 100° to a dark yellow mass. The *nitrate*, $C^{20}H^{24}N^2O.NHO^3 + \frac{1}{2}aq.$, forms monoclinic twin-crystals soluble in 26·4 pts. water. The *benzoate*, $C^{20}H^{24}N^2O.C^7H^6O^2$, crystallises in stellate groups of anhydrous prisms soluble in 163 pts. water at 15°. The *sulphate*, $2C^{20}H^{24}N^2O.SH^2O^4 + 2aq.$, dissolves in 65·5 pts. water at 13° and in 5·8 pts. alcohol (of 80 p. c.) at 11°. The *hyposulphite*, $2C^{20}H^{24}N^2O.S^2H^2O^3 + 2aq.$, forms rhombic prisms $mP\infty . m\breve{P}\infty . oP$ (?), soluble in 157 pts. water at 16°. The *chromate*, $2C^{20}H^{24}N^2O.CrH^2O^4$, is deposited on mixing the hydrochloride with a gently warmed solution of potassium dichromate, in small ochre-yellow prisms, which decompose in the moist state on exposure to light. The *phosphate*, $2C^{20}H^{24}N^2O.PH^3O^4 + 12aq.$, forms concentrically grouped prisms easily soluble in water. The *arsenate*, $2C^{20}H^{24}N^2O.AsH^3O^4 + 12aq.$, forms long prisms, easily soluble in water (Hesse). An aqueous solution of a cinchonine salt gives with *sodium sulpharsenate* a bulky precipitate soluble in excess of the reagent (Mosing, *Zeitschr. f. Chem.* [2] v. 353). The *oxalate*, $2C^{20}H^{24}N^2O.C^2H^2O^4 + 2aq.$, crystallises in large prisms soluble in 104 pts. water at 10°. The *acid succinate*, $C^{20}H^{24}N^2O.C^4H^6O^4$, crystallises in long oblique-angled needles containing $\frac{3}{2}H^2O$, or in large thick crystals with $1H^2O$, both forms melting at 110°, and dissolving easily in water. The *acid tartrate*, $C^{20}H^{24}N^2O.C^4H^6O^6 + 4aq.$, forms small prisms dissolving in 101 pts. water at 16° with acid reaction. The *neutral tartrate*, $2C^{20}H^{24}N^2O.C^4H^6O^6 + 2aq.$, is less fusible than the acid salt, has a slight alkaline reaction, and when dehydrated, quickly reabsorbs its full amount of water on exposure to the air. *Cinchonine-antimonious tartrate*, obtained by decomposing the sulphate with bario-antimonious tartrate, crystallises from water, partly in white, easily efflorescing nodules containing 24·7 p. c. water, partly in large crystals resembling saltpetre and containing from 9·8 to 10 p. c. water. The compound dried at 100° contains 26·2 to 26·5 p. c. antimony and 47·48 p. c. cinchonine. The *acid citrate*, $2C^{20}H^{24}N^2O.C^6H^8O^7 + 4aq.$, forms small prisms soluble in 55·8 pts. water at 15°. The *neutral citrate*, $3C^{20}H^{24}N^2O.C^6H^8O^7 + 4aq.$, separates on evaporating its alcoholic solution, as a colourless oil which solidifies in long concentrically grouped prisms. The *picrate*, $2C^{20}H^{24}N^2O.3C^6H^3(NO^2)^3O$, is obtained as a yellow precipitate resembling lead iodide, on mixing conchonine hydrochloride with a gently warmed solution of picric acid (Hesse).

Action of Potassium Permanganate on Cinchonine (Caventou a. Willm, *Zeitschr. f. Chem.* [2] v. 547).—When a cold-saturated solution of potassium permanganate is added by drops to a solution of about an equal quantity of cinchonine sulphate, likewise kept cool and acidulated with sulphuric acid, carbon dioxide is evolved, and the following products are formed:

1. Hydrocinchonine, $C^{20}H^{26}N^2O$.—2. Cinchotenine, an indifferent body which unites both with acids and with bases, but without forming well-defined compounds. —3. Carboxycinchonic acid.—4. A substance which reduces cupric oxide in alkaline solution. The last three are products of oxidation.

Hydrocinchonine, $C^{20}H^{26}N^2O$, melts at 268°, deflects the plane of polarisation to the left, but less strongly than cinchonine; it is insoluble in water; a litre of 90 p. c. alcohol dissolves 7·25 grm. of it at 15°; at higher temperatures it is more soluble and separates on cooling in small silky needles. It forms well-crystallised salts, soluble in water and having a bitter taste. The *platinochloride*, $C^{20}H^{26}N^2O.2HCl.PtCl^4$, forms rather large shining crystals. It is but slowly attacked by potassium permanganate.

1. *Cinchotenine*, $C^{18}H^{20}N^2O^3$, the most abundant of the oxidation products, separates from a boiling aqueous solution in silver-white silky crystals, but slightly soluble in cold water and in alcohol, even at the boiling heat. It turns the plane of polarisation to the left, but less strongly than cinchonine. It has a neutral reaction, and dissolves both in acids and in alkalis, but is insoluble in strong potash-ley. From its solution in baryta-water it is precipitated by carbonic acid. It forms a crystallisable platinochloride. With silver nitrate it forms a white precipitate and reduces the silver when heated. It is but slowly attacked by potassium permanganate even with aid of heat.

Carboxycinchonic acid, $C^{21}H^{14}N^2O^4$, is formed from cinchonine by addition of water, as well as by oxidation. Its formation appears to take place only when the evolution of carbon dioxide becomes energetic, and is perhaps analogous to that of benzoic acid by oxidation of benzene. It is moderately soluble in water, especially when hot, and crystallises in hard shining anhydrous prisms. 100 pts. alcohol dissolve 1·8 pts. of it in the cold, somewhat more than 3 pts. at the boiling heat. It is bibasic, and forms with the alkalis and with baryta, easily soluble salts, difficult to crystallise. The *cupric salt* $C^{21}H^{12}N^2O^4Cu$ is formed as an amorphous blue-green precipitate, which quickly becomes crystalline and deep blue. The *silver salt* $C^{21}H^{12}N^2O^4Ag^2$ is a very permanent crystalline precipitate. The acid likewise dissolves in hydrochloric, sulphuric acid, &c., and forms a *platinochloride* crystallising in orange-yellow laminæ sparingly soluble in water.

CINCHOTENINE. See the last article.

CINNAMEÏN. Benzyl Cinnamate. (See CINNAMIC ETHERS, p. 470.)

CINNAMENE or **CINNAMOL.** C^8H^8.—According to Berthelot (*Compt. rend.* lxiii. 518), cinnamene produced by the dry distillation of cinnamates is not identical in its physical properties with styrol from storax. Styrol is optically active, turning the plane of polarisation 3° to the left in a layer 100 mm. thick, whereas cinnamene is optically inactive. Moreover, styrol is more easily converted than cinnamene into polymerides under the influence of heat and of chemical reagents; and when mixed with $1\frac{1}{3}$ time its weight of strong sulphuric acid it gives off a larger quantity of heat, viz. 30,000 heat-units for the molecule C^8H^8, whereas cinnamene gives only three-fourths of that quantity. But the difference between the two is purely physical; in chemical properties and reactions, and therefore doubtless in the arrangement of the atoms in their molecules, they are absolutely identical.

Cinnamene (or styrol) is produced: 1. By polymerisation of acetylene. It has in fact the composition of tetracetylene, $(C^2H^2)^4$, and is formed, together with other polymerides, when acetylene is heated in a sealed glass tube over mercury to the softening point of the glass. It constitutes about $\frac{1}{5}$ of the liquid product thus obtained, passes over on fractionally distilling that liquid between 135° and 160°, and is identical in every respect with the cinnamene obtained from cinnamates (Berthelot, *Compt. rend.* lxii. 905, 947; see also ACETYLENE, p. 32).

2. When a mixture of ethylene and benzene or diphenyl is passed through a red-hot tube (Berthelot, *Jahresb.* 1866, pp. 545, 546):

$$C^6H^6 + C^2H^4 = C^8H^8 + H^2$$

and

$$C^{12}H^{10} + C^2H^4 = C^8H^8 + C^6H^6.$$

3. Together with benzene and several other hydrocarbons, when ethylene alone is passed through a red-hot porcelain tube (Berthelot, *Zeitschr. f. Chem.* [2] iv. 384).

4. Together with other hydrocarbons, by passing the vapour of ethyl-benzene (p. 292) through a red-hot tube (Berthelot, *Zeitschr. f. Chem.* [2] iv. 589):

$$C^6H^5(C^2H^5) = C^8H^8 + H^2.$$

5. By abstraction of HBr from styryl bromide, (C^8H^9Br) (produced by the action of bromine-vapour on ethyl-benzene at the boiling heat), which may be effected by heating the bromide with alcoholic potash to 180°. Under these circumstances, the cinnamene is at first converted into metacinnamene, and the product when distilled yields, above 300°, a mixture of cinnamene with an oxidised body (probably styrylic ether, $C^{16}H^{18}O$); by a second distillation the cinnamene is obtained pure. Cinnamene is also obtained, in small quantity and as a secondary product, when styryl bromide is heated with sodium, or when it is made to act on certain salts (alkaline acetates and benzoates) at 180° (Berthelot, *loc. cit.*).

Reactions.—1. Cinnamene-vapour passed through a red-hot tube is partly resolved into benzene and acetylene (or its products of condensation), according to the equation $C^8H^8 = C^6H^6 + C^2H^2$.—2. When heated in a sealed tube filled with *hydrogen*, it is resolved into benzene and ethylene; thus:

$$C^8H^8 + H^2 = C^6H^6 + C^2H^4;\ \text{and}\ 3C^8H^8 = 4C^6H^6$$

(Berthelot, *Jahresb.* 1866, p. 544).—3. A mixture of cinnamene and *ethylene* passed through a red-hot tube yields large quantities of benzene and naphthalene, the first produced by breaking up of the cinnamene molecule, as above; the second according to the equation:

$$C^8H^8 + C^2H^4 = C^{10}H^8 + 2H^2.$$

4. A mixture of cinnamene and *benzene* vapours similarly treated yields anthracene as principal product, together with smaller quantities of naphthalene and a hydrocarbon resembling diphenyl (Berthelot, *ibid.* p. 545):

$$\underset{\text{Cinnamene.}}{C^8H^8} + \underset{\text{Benzene.}}{C^6H^6} = \underset{\text{Anthracene.}}{C^{14}H^{10}} + 2H^2.$$

5. Cinnamene shaken up with an alkaline solution of *potassium permanganate* is converted into benzoic and carbonic acids (Berthelot, *ibid.* 1867, p. 337):

$$C^8H^8 + O^5 = C^7H^6O^2 + CO^2 + H^2O.$$

6. Cinnamene treated with 80 pts. of saturated aqueous *hydriodic acid* yields as principal product octane, C^8H^{18}, boiling at 115°–120°, together with small quantities of ethane and septane:

$$\underset{\text{Cinnamene.}}{C^8H^8} + 10HI = \underset{\text{Octane.}}{C^8H^{18}} + 5I^2.$$

$$\underset{\text{Cinnamene.}}{C^8H^8} + 12HI = \underset{\text{Ethane.}}{C^2H^6} + \underset{\text{Septane.}}{C^6H^{14}} + 6I^2.$$

With 20 pts. of the acid, it is converted for the most part into styryl hydride, C^8H^{10} (ethyl-phenyl?), while benzene, ethane, and a resinous hydrocarbon of high boiling point occur as secondary products:

$$C^8H^8 + 4HI = C^6H^6 + C^2H^6 + 2I^2$$

(Berthelot, *Jahresb.* 1867, p. 449).

7. When cinnamene is agitated with a concentrated solution of *iodine* in potassium iodide, and the liquid is then diluted with water, a beautifully crystallised iodide of cinnamene separates, which dissolves easily in ether and in hydrocarbons, is not decomposed by sulphurous acid and sodium carbonate, but splits up spontaneously after some time into iodine and a resinous substance (Berthelot).

8. With *bromine*, cinnamene forms the crystallised bromide $C^8H^8Br^2$ (i. 682).

9. With *chlorine*, cinnamene yields a liquid product, which is quickly converted by strong sulphuric acid into polymerides, partly volatilising without decomposition when heated above 300°, and therefore not identical with metacinnamene (Berthelot).

10. Fuming *nitric acid* acts strongly on cinnamene, separating a resinous body, and forming a solution which on evaporation deposits a similar resinous substance, insoluble in ether, remaining behind for the most part when distilled with water, and not yielding any volatile basic product by distillation with iron-filings and acetic acid. Other polymerides of acetylene exhibit a similar reaction with nitric acid (Berthelot).

The last four reactions, together with the conversion into metacinnamene by heating in closed vessels, are recommended by Berthelot (*Bull. Soc. Chim.* [2] vi. 295) for the detection and isolation of cinnamene.

For the detection of cinnamene in coal-tar—in which it is likely to occur in consequence of its formation, as above described, from benzene and other hydrocarbons at high temperatures—the crude light coal-naphtha, not yet treated with strong sulphuric acid, is agitated with soda-ley and with dilute sulphuric acid; then washed and fractionally distilled; and the portion collected after frequent rectifications between 144° and 150° is heated to 200° for several hours in a sealed tube. The contents of the tube are then distilled at about 300°, and the residue is more strongly heated, whereby a mixture of regenerated cinnamene and difficultly volatile hydrocarbons is obtained, from which the cinnamene may be separated by renewed distillation and tested as above. The liquid passing over between 144° and 150° was found to contain 2 p. c. cinnamene. Coal-tar naphtha purified in the ordinary way with strong sulphuric acid cannot contain cinnamene, since this hydrocarbon is thereby converted into polymeric modifications, which remain in the less volatile residue (Berthelot, *loc. cit.*).

Dicinnamene or *Distyrol*, $C^{16}H^{16}$, is produced, together with carbon dioxide, by heating cinnamic acid to 150°–240° with aqueous hydrobromic acid (sp. gr. 1·35), with hydrochloric acid (sp. gr. 1·12), or with sulphuric acid diluted with 2 pts. water. It unites with bromine, forming the crystalline compound $C^{16}H^{16}Br^2$. It is not converted into metacinnamene by prolonged heating to 200° (Erlenmeyer, *Ann. Ch. Pharm.* cxxxv. 122).

CINNAMIC ACID. $C^9H^8O^2$.—Produced: 1. According to Harnitz-Harnitzky (*Ann. Ch. Pharm.* cxi. 192), by the action of chlorethylidene (obtained by the action of carbonyl chloride on aldehyde) on barium benzoate:

$$C^2H^3Cl + C^7H^5O^2Ba' = Ba'Cl + C^9H^8O^2.$$

Kraut (*Zeitschr. f. Chem.* [2] v. 147) did not obtain cinnamic acid by this reaction. —2. By the action of carbon dioxide and sodium on bromocinnamene dissolved in ether (just as benzoic acid is formed from bromobenzene):

$$C^8H^7Br + CO^2 + Na^2 = NaBr + C^9H^7O^2Na$$

(Th. Swarts, *Ann. Ch. Pharm.* cxxxvii. 229; *Bull. Soc. Chim.* [2] vi. 61).

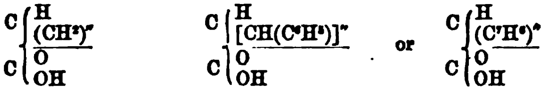
3. By the action of bromine on hydrocinnamic acid (Glaser, *Jahresb.* 1866, p. 367):

$$C^9H^{10}O^2 + Br^2 = 2HBr + C^9H^8O^2.$$

The decomposition of cinnamic acid by fusion with potash into benzoic and acetic acids, with evolution of hydrogen (i. 984), according to the equation

$$C^9H^8O^2 + 2KOH = C^7H^5KO^2 + C^2H^3KO^2 + H^2,$$

is analogous to that of the acrylic acids (p. 41), and shows that cinnamic acid may be regarded as phenyl-acrylic acid:



$$C\begin{cases}H\\(CH^2)''\end{cases} \quad C\begin{cases}O\\OH\end{cases} \qquad C\begin{cases}H\\ [CH(C^6H^5)]''\end{cases} \quad C\begin{cases}O\\OH\end{cases} \quad \text{or} \quad C\begin{cases}H\\(C^7H^6)''\end{cases} \quad C\begin{cases}O\\OH\end{cases}$$

Acrylic. Phenyl-acrylic or Cinnamic.

This view of its constitution is also in accordance with its formation from acetyl chloride and benzoic aldehyde (i. 983), and from chlorethylidene and barium benzoate.

Reactions.—1. Cinnamic acid shaken up with *water* and *sodium-amalgam*, in the proportion of 1 at. sodium to 1 mol. cinnamic acid, is converted into hydrocinnamic acid, $C^9H^{10}O^2$ (Erlenmeyer, *Ann. Ch. Pharm.* cxxxvii. 227).—2. It is also converted into hydrocinnamic acid by heating it to 100° with very strong aqueous *hydriodic* acid (Popoff, *Zeitschr. f. Chem.* [2] i. 111):

$$C^9H^8O^2 + 2HI = C^9H^{10}O^2 + I^2.$$

3. When gradually heated to 190°–200° with *hydrochloric acid*, it yields an indifferent chlorinated oil, probably C^8H^9Cl, together with carbon dioxide; and reacts in like manner with *hydrobromic acid* (Schwarts, *loc. cit.*). According to Erlenmeyer, hydrochloric acid of sp. gr. 1·12 and hydrobromic acid of sp. gr. 1·85 convert it at 150°–240° into dicinnamene, $C^{16}H^{16}$.

4. *Heated* with *water* to 180°–200° for about a week, it is decomposed, with formation of cinnamene (Schwarts). According to Erlenmeyer, it is not decomposed by heating with water to 230°, but when heated in the dry state to 240°, it slowly gives off carbon dioxide.

5. *Bromine-vapour* is absorbed by cinnamic acid at ordinary temperatures or at 100°, with formation of dibromo-hydrocinnamic acid, $C^9H^8Br^2O^2$ (A. Schmitt, *Ann. Ch. Pharm.* cxxvii. 319).

6. Cinnamic acid unites directly with *hypochlorous acid*, forming phenyl-chlorolactic acid, $C^9H^9ClO^3$:

$$\underset{\text{Phenyl-acrylic.}}{C^3H^3(C^6H^5)O^2} + HClO = \underset{\text{Phenyl-chlorolactic.}}{C^3H^4(C^6H^5)ClO^3}$$

With free cinnamic acid this reaction does not take place very readily; but when chlorine is passed in a slow stream into a dilute solution of cinnamic acid in sodium carbonate till the liquid loses its alkaline reaction and acquires bleaching properties, phenyl-chlorolactic acid is easily formed. The solution freed from excess of chlorine and hypochlorous acid by sulphurous acid, and then treated with hydrochloric acid, yields phenyl-chlorolactic acid in prismatic crystals. This acid treated with *sodium-amalgam* is converted into phenyl-lactic acid, $C^9H^{10}O^3$, or phenyl-oxypropionic acid, $C^9H^9(HO)O^2$, which, when treated with *hydrochloric*, *hydrobromic*, or *hydriodic acid*, takes up Cl, Br, or I in place of HO, forming phenyl-chloropropionic acid, $C^9H^9ClO^2$, &c. In like manner, phenyl-chlorolactic acid, $C^9H^9ClO^3$ or $C^9H^8(HO)ClO^2$, treated with *hydrochloric acid*, takes up Cl in place of HO, forming phenyl-dichloropropionic acid, $C^9H^8Cl^2O^2$; and similarly with *hydrobromic acid* it forms phenyl-chlorobromopropionic acid, $C^9H^8ClBrO^2$. Lastly, phenyl-chlorolactic acid, treated with *alkalis*, yields a chloride of alkali-metal, together with phenyl-oxyacrylic or oxycinnamic acid:

$$C^9H^9ClO^3 + KOH = C^9H^8O^3 + KCl + H^2O.$$

The relation of these several derivatives to cinnamic acid is exhibited by the following formulæ:

Phenyl-acrylic (cinnamic) acid	$C^6H^5.C^3H^3O^2$
Phenyl-chlorolactic acid	$C^6H^5.C^3H^3(ClHO)O^2$
Phenyl-dichloropropionic acid	$C^6H^5.C^3H^3(Cl^2)O^2$
Phenyl-bromochloropropionic acid	$C^6H^5.C^3H^3(BrCl)O^2$
Phenyl-lactic acid	$C^6H^5.C^3H^3(HOH)O^2$
Phenyl-chloropropionic acid	$C^6H^5.C^3H^3(HCl)O^2$
Phenyl-oxyacrylic (oxycinnamic) acid . . .	$C^6H^5.C^3H^3(O)O^2$

Brominated and iodated compounds analogous to the chlorinated bodies in the above table are formed by precisely similar reactions, and the monobrominated and monoiodated propionic acids are also converted by alkalis into oxycinnamic acid (Glaser, *Ann. Ch. Pharm.* cxlvii. 78; *Zeitschr. f. Chem.* [2] iii. 65; iv. 131; *Jahresb.* 1867, p. 418). For details respecting these acids, see LACTIC ACID and PROPIONIC ACID.

Bromocinnamic Acid. $C^9H^7BrO^2$ (Glaser, *Ann. Ch. Pharm.* cxliii. 325; *Jahresb.* 1866, p. 367).—When bromine acts at ordinary temperatures on hydrocinnamic acid, two brominated acids are formed by successive substitution, viz. $C^9H^9BrO^2$ and $C^9H^8Br^2O^2$, the latter of which is isomeric with the dibromide of cinnamic acid (or dibromo-hydrocinnamic acid), which Schmitt obtained by direct addition of bromine to cinnamic acid (p. 467). This dibrominated acid treated with alcoholic potash solution gives up HBr and yields two isomeric monobromocinnamic acids, $C^9H^7BrO^2$. To prepare these acids, the crude product of the action of bromine-vapour on cinnamic acid is dissolved in a small quantity of boiling alcohol, and an alcoholic solution of potash is added to it by portions in slight excess. It then deposits, first, white crystalline flocks of α-bromocinnamic acid, then an oily mixture, and ultimately nearly pure β-bromocinnamic acid; the complete separation of the two isomeric acids must be effected by fractional precipitation.

α-Bromocinnamic acid, $C^9H^7BrO^2$, separated from its ammonium salt, crystallises from boiling water in long shining four-sided needles, soluble in all proportions of alcohol, easily soluble also in alcoholic ether, less soluble in pure ether. It melts at 130°–131°, crystallises in needles on cooling, and distils for the most part without decomposition. The *ammonium salt* $C^9H^6BrO^2.NH^4$ forms flat needles generally united in arborescent groups, moderately soluble in water and in alcohol. The *potassium salt* crystallises in needles easily soluble in water and in alcohol. The *silver salt* $C^9H^6BrO^2Ag$ is sparingly soluble in water, and is resolved by heating with water to 150° into the free acid and a basic salt, without formation of silver bromide. The *barium salt* $(C^9H^6BrO^2)^2Ba$ crystallises in thin rhombic laminæ, slightly soluble in cold water, insoluble in alcohol. The *zinc salt* forms laminæ easily soluble in hot water; the *cadmium salt* large flat shining prisms; the *lead salt* crystallises from hot water in thin rhombic laminæ.

α-Bromocinnamic acid is converted by contact with bromine into an acid richer in bromine, melting at 132°, and crystallising in needles. By sodium-amalgam it is converted into hydrocinnamic acid:

$$C^9H^7BrO^2 + 2H^2 = HBr + C^9H^{10}O^2.$$

β-Bromocinnamic acid, $C^9H^7BrO^2$, purified by fractional precipitation as above mentioned, is a light snow-white powder composed of six-sided laminæ. It is easily soluble in boiling water, and separates therefrom in large flat six-sided crystals, from ether in well-defined thick prisms. It melts at 120°, and is converted by distillation or by boiling with fuming hydriodic acid into α-bromocinnamic acid. Heated to 180° with weak soda-ley, it is resolved into carbon dioxide and a non-brominated oil boiling at about 160°. It is also converted by sodium-amalgam into hydrocinnamic acid. Its salts are totally different from those of the α-acid. The *potassium salt* $C^9H^6BrO^2K$ forms slender very deliquescent needles easily soluble in alcohol. The *silver salt* $C^9H^6BrO^2Ag$ is a white curdy precipitate, which becomes crystalline on standing and is decomposed by boiling; at 120° it is resolved into the free β-acid and a basic salt; at 170° into α-bromocinnamic acid, carbon dioxide, silver bromide, and an aromatic oil.

β-Bromocinnamic acid exposed to the action of bromine-vapour is converted into a crystalline acid richer in bromine, which melts at 45° and 48°, and is decomposed by boiling water, with formation of a volatile oil having an odour different from that of the acid itself.

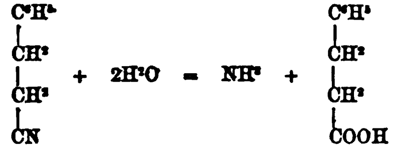
Hydrocinnamic Acid. $C^9H^{10}O^2$. *Homotoluic acid*, *Cumoylic acid*, *Phenyl-propionic acid* (Erlenmeyer, *Zeitschr. Ch. Pharm.* 1862, p. 170; 1863, p. 307; *Zeitschr. f. Chem.* 1866, p. 206; *Ann. Ch. Pharm.* cxxxvii. 327. A. Schmitt, *ibid.* cxxvii. 319. Popoff, *Bull. Soc. Chim.* [2] iv. 375. Fittig, *Zeitschr. f. Chem.* 1869,

p. 166).—This acid, isomeric with xylic, and homologous (in composition at least) with toluic acid, is produced: 1. By the action of sodium-amalgam on cinnamic acid. Pulverised cinnamic acid is agitated in a stoppered vessel with 20 to 24 times its weight of water and a quantity of sodium-amalgam containing 1 at. sodium to 1 mol. cinnamic acid, till the liquid becomes neutral or nearly so; a second and somewhat larger quantity of sodium-amalgam is then added; and the reaction is continued, with frequent agitation, till hydrogen gas is given off in regular bubbles. The resulting sodium salt is then neutralised with sulphuric acid; the solution is evaporated; the mother-liquor decanted from the crystallised sodium sulphate is supersaturated with sulphuric acid; and the hydrocinnamic acid which separates as an oil, but soon solidifies, is pulverised, washed with water, then distilled, and dissolved in boiling water, from which it separates at low temperatures in needles, or from a solution saturated at the boiling heat, as an oil which afterwards solidifies (Erlenmeyer).

2. By the action of sodium-amalgam on dibromohydrocinnamic acid, $C^9H^8Br^2O^2$, which is produced by direct addition of bromine to cinnamic acid (Schmitt).

3. By heating cinnamic acid with concentrated hydriodic acid: $C^9H^8O^2 + 2HI = C^9H^{10}O^2 + I^2$ (Popoff).

4. From ethyl-benzene, $C^6H^5.CH^2CH^3$, by passing chlorine into that compound at the boiling heat, whereby it is converted into phenyl-ethyl chloride, $C^6H^5.CH^2CH^2Cl$; converting this chloride into the corresponding cyanide by heating it with potassium cyanide and alcohol in a flask provided with an upright condensing tube; and heating the decanted alcoholic solution of phenyl-ethyl cyanide with solid caustic potash in a similar apparatus as long as ammonia is given off. On subsequently distilling off the alcohol, acidulating the remaining liquid with sulphuric acid, repeatedly agitating with ether, and distilling off the ether from the resulting solution, a yellow liquid acid is left, which solidifies after standing and repeated agitation with cold water. By converting this acid into a calcium salt, and decomposing the latter with hydrochloric acid, an acid is obtained identical in every respect with the hydrocinnamic acid obtained by the preceding methods. Its formation from phenyl-ethyl cyanide is represented by the equation:



$$\begin{array}{l} C^6H^5 \\ | \\ CH^2 \\ | \\ CH^2 \\ | \\ CN \end{array} + 2H^2O = NH^3 + \begin{array}{l} C^6H^5 \\ | \\ CH^2 \\ | \\ CH^2 \\ | \\ COOH \end{array}$$

Phenyl-ethyl cyanide. Hydrocinnamic acid.

This reaction is exactly similar to that by which ethyl cyanide is converted into propionic acid, and shows that hydrocinnamic acid has the constitution of phenyl-propionic acid (Fittig).

Hydrocinnamic acid melts at 47° (Erlenmeyer), at 46·5° (Fittig), and boils at 280° under a pressure of 754 mm. (Erlenmeyer). Its vapours condense to a liquid, which when at perfect rest may be cooled to 25° without solidifying; but when touched with a solid body immediately solidifies to a radiate mass of long needles, the temperature at the same time rising to 42°. It dissolves in 168 pts. water at 20°, much more easily in boiling water, and volatilises with vapour of water; it dissolves in alcohol, and separates therefrom in prisms apparently belonging to the monoclinic system; also in ether, chloroform, benzol, carbon bisulphide, and glacial acetic acid. Its salts are mostly crystallisable, and the solution of the potassium salt is not precipitated by salts of calcium, barium, magnesium, nickel, cobalt, or manganese; with silver nitrate, zinc sulphate, cupric nitrate, mercuric chloride, ferric chloride, and chromic chloride it gives flocculent precipitates; with lead acetate a glutinous precipitate. The *silver salt* $C^9H^9O^2Ag$ crystallises from water in nacreous laminæ; the *potassium*, *barium*, *calcium*, and *lead salts* in needles; the *copper salt* is a pale green powder (Erlenmeyer). The *calcium salt* dried over sulphuric acid contains, according to Fittig, $2(C^9H^9O^2)^2Ca.3H^2O$.

Methyl hydrocinnamate, $C^9H^9O^2.CH^3$, is a liquid having a peculiar odour, a sp. gr. of 1·0455 at 0°, and 1·0180 at 49°, and boiling at 238°–239°. The *ethylic ether* $C^9H^9O^2.C^2H^5$ smells like pine-apples, has a sp. gr. of 1·0343 at 0°, 0·9925 at 49°, and boils at 247°–249°. The *amylic ether* $C^9H^9O^2.C^5H^{11}$ has a faint and stupefying odour, a sp. gr. of 0·9807 at 0°, 0·9520 at 49°, and boils at 291°–293°.

Hydrocinnamic acid is oxidised by chromic acid mixture, giving off carbon dioxide even at ordinary temperatures, and on distilling the liquid benzoic acid is given off, together with an oily body. Heated with soda-lime or potassium hydrate, it gives off first benzoic acid, and afterwards a yellow liquid containing hydrocarbons (toluene), and perhaps also ketones (Erlenmeyer).

Dibromohydrocinnamic or *Dibromo-phenylpropionic acid*, $C^9H^8Br^2O^2$, is formed by direct combination when bromine-vapour is passed over cinnamic acid at 100°; liquid bromine is less readily absorbed. The brominated acid is insoluble in cold water, easily soluble in ether and in alcohol, crystallises from the latter in colourless rhombic laminæ, has a bitter taste, and is not volatile without decomposition. Its *barium salt* $(C^9H^7Br^2O^2)^2Ba$, obtained by saturation, is easily decomposible, dissolves readily in water, aclohol, and ether, and crystallises in microscopic four-sided plates. The *sodium salt* $C^9H^7Br^2O^2Na$ is somewhat more stable; its solution gives precipitates with lead acetate, stannic chloride, and mercurous nitrate. The acid, $C^9H^8Br^2O^2$, boiled with water, gives off a neutral brominated oil having an odour of hyacinths, and the residual liquid deposits a crystalline body, difficult to purify, but probably consisting of $C^9H^9BrO^2$. The dibrominated acid is converted by sodium-amalgam into hydrocinnamic acid, together with a small quantity of another acid (not yet analysed), which is soluble in water and crystallises in large prisms (A. Schmitt, *loc. cit.*).

Oxycinnamic or **Phenyl-oxyacrylic acid,** $C^9H^8O^3 = C^6H^5.C^3H^3(O)O^2$ or $C^6H^5.C^3H^2(HO)O^2$, is produced by the action of alkalis on phenyl-chlorolactic or phenyl-bromolactic acid (p. 467). To prepare it, the alcoholic solution of the chlorinated or brominated acid is stirred up with an alcoholic solution of potash, soda, or ammonia, in sufficient quantity to render the liquid alkaline; the precipitate, consisting of metallic chloride or bromide, together with a salt of oxycinnamic acid, is collected on a filter after a few hours, washed with cold alcohol, and then digested with boiling alcohol, which dissolves out the oxycinnamate, and deposits it in the crystalline form on cooling. From the moderately dilute solution of this salt, the acid $C^9H^8O^3$ is precipitated by a stronger acid, as an oil which when cooled nearly to 0° solidifies in shining crystalline spangles. It is very unstable, changing soon after preparation into a resinous substance, with evolution of carbon dioxide, and being resolved by boiling with water into carbon dioxide and a volatile oil, probably oxycinnamene, C^8H^8O. It is resinised by heating with hydrochloric or hydrobromic acid.

Potassium oxycinnamate, $C^9H^7O^3K$, forms nacreous laminæ easily soluble in hot water, but gradually decomposing in the aqueous solution into carbon dioxide and a colourless resin. The *sodium salt* $C^9H^7O^3Na$ crystallises in tufts of flat needles; the *ammonium salt* in small prisms. The *silver salt* $C^9H^7O^3Ag$ is sparingly soluble, and may be obtained by precipitation, or directly from phenyl-chlorolactic acid by slightly supersaturating with ammonia, and cautiously adding silver nitrate, so as first to decompose the ammonium chloride in the solution, and then precipitate the silver oxycinnamate from the filtrate. From a solution in boiling water, prepared in the dark and rapidly cooled, it is deposited as a crystalline powder consisting of six-sided laminæ, easily altered by heat and light. The *barium salt* is obtained by double decomposition as a white precipitate which crystallises from boiling dilute alcohol in small needles. The *ethylic ether* $C^9H^7O^3.C^2H^5$, formed by the action of ethyl-iodide on the silver salt, is a liquid of agreeable fruity odour, and boiling at 279·5° (corr.), with partial decomposition. When boiled with baryta-water it is decomposed, with separation of barium carbonate.

Thiocinnamic Acid. C^9H^8OS.—Cinnamyl chloride, C^9H^7OCl, acts strongly on lead sulphethylate (mercaptide), forming lead-chloride, and an oil soluble in ether but insoluble in water, which boils with partial decomposition at 250°, and when boiled with alcoholic potassium sulphydrate, gives off mercaptan, and yields crystalline nodules of potassium thiocinnamate, C^9H^7OSK (Engelhardt, Latschinoff a. Malyscheff, *Zeitschr. f. Chem.* [2] iv. 359).

CINNAMIC ETHERS. *Ethyl Nitrocinnamate*, $C^9H^6(NO^2)O^2.C^2H^5$, is easily produced by dissolving ethyl cinnamate in very concentrated nitric acid. Treated with tin and hydrochloric acid, it yields colourless crystals consisting of a compound of stannous chloride with the hydrochloride of ethyl amido-cinnamate, $2[C^9H^6(NH^2)O^2.C^2H^5.HCl].SnCl^2 + 3aq.$, which, when freed from tin by hydrogen sulphide, yields colourless crystals of the *hydrochloride of ethyl amidocinnamate* (J. v. Rossum, *Jahresb.* 1866, p. 365).

Benzyl Cinnamate. $C^{16}H^{14}O^2 = C^9H^7O^2.C^7H^7$. *Cinnameïn* (i. 980).—This ether is obtained in the pure state by boiling a mixture of benzyl chloride, alcohol, and well-dried sodium cinnamate in a flask with upright condenser for several hours, till no more sodium cinnamate separates out on cooling. On distilling off the alcohol, adding water, washing the pasty precipitate with an alkaline solution to remove free cinnamic acid, then agitating with ether, and evaporating the ethereal solution over the water-bath, an oily liquid remains, which when distilled in a vacuum yields at 100° a thin mobile liquid (benzyl alcohol and benzyl chloride), and between 225° and 235° benzyl cinnamate in the form of a thick oil, which gradually solidifies at 0°, and may be completely purified by dissolving it in alcohol at a temperature below 40° and cooling the solution to a low temperature. It is always partially decomposed during preparation into cinnamic acid and benzyl alcohol, the quantity thus decomposed being greater the longer the heating is continued.

Pure benzyl cinnamate forms short, shining white prisms having a pleasant aromatic odour; it melts at 39°, and may then remain liquid for several hours even at 0°. At about 350° it decomposes, with formation of cinnamic acid and oily substances. It dissolves easily in alcohol and ether, and is quickly decomposed by alcoholic potash, even in the cold. Frémy's metacinnameïn (i. 980) is probably pure benzyl cinnamate (Grimaux, *Zeitschr. f. Chem.* [2] v. 157).

According to Delafontaine (*ibid.* p. 156), the cinnameïn obtained from Peru balsam is a mixture of benzyl cinnamate and cinnyl cinnamate or styracin. When heated with alcoholic potash it yields potassium cinnamate, and an oil, which is resolved for the most part by fractional distillation into benzylic and cinnylic alcohols.

CINNAMIDE, $C^9H^9NO = C^9H^7O.NH^2$, is most conveniently prepared by treating cinnamyl chloride with concentrated aqueous ammonia, washing the resulting crystalline pulp with cold water, and recrystallising it from boiling water, from which it separates by slow cooling in dazzling white crystals; from alcohol it crystallises in needles; in ether it is but sparingly soluble. It is inodorous, has a faintly bitter taste, melts at 141·5°, and when boiled with hydrochloric acid appears to form an unstable hydrochloride. Boiled with mercuric oxide, it yields white pulverulent mercuric cinnamide, $(C^9H^8NO)^2Hg$ (J. v. Rossum, *Zeitschr. f. Chem.* [2] ii. 362).

Thiocinnamide, $C^9H^9NS = C^9H^7S.NH^2$, separates on treating an ammoniacal solution of cinnamonitrile with hydrogen sulphide and evaporating, and crystallises from water in yellow laminar crystals (v. Rossum).

CINNAMONITRILE, C^9H^7N, is produced by heating cinnamide with an equivalent quantity of phosphorus pentachloride, distilling off the resulting phosphorus oxychloride, and heating the residue with potash. It crystallises at low temperatures, melts at 11°, boils at 254°–255°, dissolves easily in alcohol, but is insoluble in water (v. Rossum).

CITRACETIC ACID. A tribasic acid formed, together with aceconitic acid (p. 2), by the action of sodium on heated ethyl bromacetate. Its composition has not been determined, but appears not to differ much from that of aceconitic acid. Its *tribaric salt* has a strong alkaline reaction; the *silver* and *lead salts* are amorphous precipitates soluble in water (Baeyer, *Zeitschr. Ch. Pharm.* 1864, p. 712).

CITRACONIC ACID. $C^5H^6O^4 = (C^3H^4)^{iv}(CO^2H)^2$.—This, like the isomeric compounds itaconic and mesaconic acids, is a bibasic acid, having two unsaturated units of affinity, and therefore capable of uniting directly with 2 at. hydrogen, chlorine, bromine, iodine, &c., or with 1 mol. HCl, HBr, HClO, &c., thereby producing saturated compounds. Treated with *water* and *sodium-amalgam*, it takes up 2 at. hydrogen and is converted into pyrotartaric acid, $C^5H^8O^4$. It unites at ordinary temperatures with 2 at. *bromine*, forming citradibromopyrotartaric acid, $C^5H^6Br^2O^4$, isomeric with itadibromopyrotartaric acid (Kekulé, *Jahresb.* 1862, p. 313). See PYROTARTARIC ACID, iv. 774; also in this volume. With *hydrochloric acid* it forms citramonochloropyrotartaric acid, $C^5H^7ClO^4$, which however is most readily formed by heating citraconic anhydride, $C^5H^4O^3$, with concentrated hydrochloric acid to 120°. The anhydride heated with fuming *hydriodic acid* is converted into pyrotartaric acid, but it is probable that a mono-iodopyrotartaric acid, $C^5H^7IO^4$, is formed as an intermediate product, though it has not been isolated (Swarts, *Jahresb.* 1866, p. 406). A dilute solution of citraconic acid neutralised with baryta and agitated with *hypochlorous acid*, is converted into the barium salt of chlorocitramalic acid, $C^5H^7ClO^5 = C^5H^6O^4 + HClO$ (Carius, *Ann. Ch. Pharm.* cxxvi. 195).

The difference of structure between the three isomeric acids, citraconic, itaconic, and mesaconic, has been explained in the article ACIDS, ORGANIC, pp. 48, 49.

Citraconates.—The *acid barium salt* $(C^5H^5O^4)^2Ba$ crystallises in fine silky needles. The *neutral barium salt* $C^5H^4O^4Ba$ (at 100°) is deposited as a crystalline powder on cooling a solution of barium carbonate in citraconic acid. This *acid calcium salt*

$(C^5H^5O^4)^2Ca + 3aq.$ forms laminæ permanent in the air, blackening and decomposing at 140°. The *neutral salt* is obtained as an amorphous powder on evaporating the acid saturated with lime-water; and on dissolving this powder in the exact quantity of water required, at ordinary temperatures, and leaving the solution to evaporate, the salt separates in step-shaped or radially grouped needle-shaped crystals having a nacreous lustre and consisting of $C^5H^4O^4Ca + 5aq.$ (Kämmerer, *Zeitschr. f. Chem.* [2] v. 252). The *acid lead salt* $(C^5H^5O^4)^2Pb$ (at 140°) separates in small yellowish crystals from a solution of the neutral salt in a large excess of citraconic acid. The *neutral lead salt* $C^5H^4O^4Pb$ is obtained on adding lead acetate to citraconic acid containing a little ammonia, as a white precipitate becoming crystalline on boiling. The crystals are anhydrous. The mother-liquor on cooling deposits a brown powder containing 1 mol. H^2O. The precipitate formed by neutral lead-acetate in a neutral solution of ammonium citraconate appears gummy when dried, and contains $2H^2O$; when boiled in the liquid it is converted into the anhydrous crystalline salt. On dropping a solution of an alkaline citraconate into a boiling solution of basic lead acetate, a crystalline pulverulent basic lead salt is precipitated, which is nearly insoluble in water, and contains $C^5H^4O^4Pb.PbO$ (Otto, *Jahresb.* 1863, p. 384). Acid *strontium citraconate*, $(C^5H^4O^4)^2Sr + 3aq.$, forms large colourless prisms, often truncated on the longitudinal edges. The *neutral salt* crystallises in a confused mass, and effloresces during the evaporation of its solution.

CITRIC ACID. $C^6H^8O^7 = (C^3H^4)^{iv}\left\{\begin{matrix}OH\\(COOH)^3\end{matrix}\right.$.—To obtain an exportable material for the manufacture of citric acid, Perret (*Bull. Soc. Chim.* [2] v. 42) treats clarified lemon-juice with excess of magnesia; washes the resulting insoluble granulo-crystalline magnesium salt with cold water; redissolves it in hot lemon-juice; and evaporates the solution rapidly, whereby a bibasic magnesium citrate, $C^6H^6O^7Mg''$, is obtained in a form convenient for exportation to the manufactories. G. Schnitzer (*Chem. Centr.* 1868, p. 272) recommends that the warmed fresh lemon-juice be mixed with a quantity of lime or chalk not quite sufficient to neutralise the acid reaction, because an excess of lime likewise precipitates those constituents of the juice which excite fermentation and occasion loss of citric acid. The calcium citrate precipitated as above may, after once washing and rapid drying, be kept for a long time without decomposition. F. Rowe (*Chem. News*, xiii. 40) dilutes the concentrated lemon-juice imported from Sicily with water, to facilitate the clarification. He also removes the injurious excess of sulphuric acid which accumulates in the concentrated solutions of citric acid obtained by decomposition of the calcium salt, by renewed treatment with lime, whereby flocculent matters consisting of gypsum and phosphates, which interfere with the crystallisation, are likewise removed. A great improvement introduced by E. A. Pontifex in the manufacture of citric acid (also in that of tartaric acid) is the use of a vacuum-pan for the final evaporation of the solutions (see Richardson and Watts's *Chemical Technology*, pt. v. p. 142).

Decompositions.—Citric acid heated to 160° in a sealed tube for several days with 8 to 10 times its weight of water is slowly resolved into itaconic acid (perhaps with small quantities of mesaconic acid), carbon dioxide, and water; the decomposition is accelerated by the presence of sulphuric acid:

$$C^6H^8O^7 = C^5H^6O^4 + CO^2 + H^2O$$

(Morkownikoff a. Purgold, *Zeitschr. f. Chem.* [2] iii. 264).

Robiquet showed that when strong sulphuric acid is poured upon dried citric acid, carbon monoxide is evolved, but that if the temperature be raised above 40°, acetone and carbon dioxide are given off (i. 996). If the liquid be freed from sulphuric acid by lead carbonate, and the filtrate partially saturated with barium carbonate, the resulting solution, evaporated below 40°, yields yellow crystals of a barium salt containing $(C^5H^7SO^5)^2Ba$. If the acetone be left out of consideration, the decomposition of citric acid by sulphuric acid may be represented by the equation:

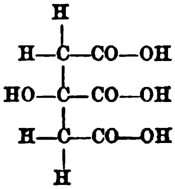
$$3C^6H^8O^7 + 2H^2SO^4 = 2C^5H^8SO^5 + 5CO^2 + 3CO + 6H^2O.$$

The solution of the acid barium salt heated with baryta-water becomes turbid, from separation of barium carbonate, and the filtrate, freed from excess of baryta by carbonic acid and a second filtration, yields by evaporation white needles of another barium salt, $(C^3H^5SO^4)^2Ba$ (C. Wilde, *Ann. Ch. Pharm.* cxxvii. 170). A solution of citric acid in absolute alcohol treated with *sodium* is converted into the sodium salt of hydrocitric acid, $C^6H^{10}O^7$ (Kämmerer, *Zeitschr. f. Chem.* [2] ii. 709).

According to Chapman a. Smith (*Laboratory*, i. 39), a solution of a citrate boiled with strongly alkaline *potassium permanganate* reduces the latter only to manganate, the liquid gradually acquiring a permanent green colour, whereas tartrates under similar circumstances reduce the permanganic acid to manganese dioxide, which is precipitated. According to Wimmel, on the other hand (*Zeitschr. f. Chem.* [2] v. 286), citrates effect the reduction to manganese dioxide as well as tartrates, only more slowly.

Constitution and Basicity.—Citric acid contains 4 atoms of replaceable hydrogen, of which three are easily replaced by metals, the fourth only by acid radicles, such as acetyl (p. 38): hence it is regarded as tetratomic and tribasic, and represented by the formula

$$(C^3H^4)^{iv}\left\{\begin{matrix}OH\\(COOH)^3\end{matrix}\right. \qquad \text{or}$$



A few quadrimetallic citrates are however known, and accordingly citric acid is by some chemists regarded as quadribasic. According to Schiff (*Jahresb.* 1862, p. 312), a quadribasic cupric salt $C^6H^4O^7Cu^2$ [$\overset{''}{Cu}{}^2 = H^4$] is produced by drying the ordinary basic salt $(C^6H^5O^7)^2Cu^3.CuH^2O^2$ + 2aq. (i. 998). The same chemist describes a ferric citrate, $C^6H^4FeO^8$, or perhaps $C^6H^4(FeO)^{iv}O^7$, obtained by desiccation of the pharmaceutical ammonio-citrate of iron. By dissolving ferric hydrate at 60° in citric acid, a brown liquid is obtained which dries up to the normal ferric salt $(C^6H^5O^7)^2(Fe^2)^{vi}$ + 6aq.

An amorphous *biplumbic salt* $C^6H^4O^7Pb^2$ + aq. is obtained by dropping a neutralised or nearly neutralised solution of citric acid into excess of a boiling solution of basic lead acetate, boiling the solution for several hours, with addition of de-aërated water, and washing the precipitate by decantation: it gives off its water at 200°. A *basic salt* $(C^6H^5O^7)^2Pb^3.2PbO$ + 3aq. (at 100°) is obtained by boiling ammonium citrate with basic lead acetate for several hours; it gives off its water at 150° (R. Otto, *Ann. Ch. Pharm.* cxxvii. 175).

Yttrium Citrates.—The *tri-yttric salt* $(C^6H^5O^7)^2Y^3$ + 14aq. is obtained on mixing sodium citrate with yttrium acetate, as a bulky crystalline precipitate, soluble in excess of the sodium salt, more soluble in cold than in hot water, easily soluble in dilute acetic acid, mineral acids, ammonia, sal-ammoniac, cold potash-ley, and, when recently precipitated, also in warm aqueous citric acid. On heating the citric acid solution to boiling, a tri-yttric citrate separates out with 7 mol. water; and on evaporating the same solution at a temperature not above 30°, the *di-yttric salt* $C^6H^6O^7Y^2$ + 4aq. crystallises out in small laminæ.

An *ammonio-bismuth citrate*, used in medicine, is obtained by dissolving precipitated bismuth citrate in aqueous ammonia (not in excess) and leaving the solution to dry upon glass plates. It then forms translucent crusts, said to contain $C^{12}H^{16}O^{11}.Bi^2O^3(NH^4)^2O$ + 5aq., or perhaps $(C^6H^5O^7)^2(Bi^2O)^{iv}(NH^4)^2$ + 5aq. (N. G. Bartlett, *Chem. News*, xi. 28).

Observations on the composition and crystalline forms of several citrates have lately been published by H. Kämmerer (*Zeitschr. f. Chem.* [2] v. 234).

Ethylic Acetyl-citrate, $C^{14}H^{22}O^8 = (C^3H^4)^{iv}\left\{\begin{matrix}OC^2H^3O\\(COOC^2H^5)^3\end{matrix}\right.$, is formed by heating 1 mol. ethyl citrate, $C^3H^4\left\{\begin{matrix}OH\\(CO^2C^2H^5)^3\end{matrix}\right.$, with 2 mol. acetyl chloride, C^2H^3OCl, and remains, after driving off the volatile products, as a yellowish oil, not miscible with water, but easily soluble in alcohol and ether. It does not solidify at −20°; distils, for the most part unaltered, at 288° (corr.). By boiling with potash it is resolved into alcohol, acetic acid, and citric acid (Wislicenus, *Ann. Ch. Pharm.* cxxix. 175).

Hydrocitric Acid. $C^6H^{10}O^7$ (Kämmerer, *Zeitschr. f. Chem.* [2] ii. 709).—The sodium salt of this acid is produced by leaving a saturated solution of citric acid in absolute alcohol in contact with small pieces of sodium (3 mol. sodium to 1 mol. of the acid) for several days, or by the action of sodium on citric acid suspended in ether perfectly free from water and alcohol. On evaporating off the alcohol or ether, dissolving the sodium salt in water, precipitating with lead-acetate, decomposing the lead-salt with hydrogen sulphide, and evaporating the filtrate over sulphuric acid, hydrocitric acid gradually separates in a mass of small prisms gradually becoming opaque and assuming the aspect of porcelain. It is insoluble in alcohol and ether, melts at 100°, crystallises again on exposure to the air, and then deliquesces. The solution gives with lead acetate a white amorphous precipitate, becoming crystalline when warmed, insoluble in water and in acetic acid. The neutralised acid gives white precipitates with the chlorides of calcium, barium, and zinc, pale green with cupric sulphate, light yellow with ferric chloride.

Hydrocitric acid is tribasic. Its *sodium salt* $2C^6H^7O^7Na^3 + 5aq.$ crystallises in rhombic prisms; the *barium salt* contains $(C^6H^7O^7)^2Ba^3 + 5aq.$, the *calcium salt* $(C^6H^7O^7)^2Ca^3 . 6aq.$, the *lead salt* $(C^6H^7O^7)^2Pb^3$ (at 100°). The *silver salt* $C^6H^7O^7Na^3 + aq.$ (at 60°) is amorphous, easily reducible, and melts to a viscid mass when heated with water.

Hydrocitric acid yields by dry distillation a pyro-acid, forming a deliquescent potassium salt, which is precipitated by barium chloride, but not by calcium chloride; its lead-salt melts under boiling water to a viscid liquid.

COBALT. *Atomic Weight.*—Russell (*Chem. Soc. J.* [2] i. 51) has determined the atomic weight of this metal by reducing the monoxide CoO (prepared by strongly igniting cobaltoso-cobaltic oxide in a stream of carbon dioxide) to the metallic state in an atmosphere of hydrogen. The mean of a considerable number of experiments gave for the proportion of metal in the monoxide, 78·5926 p. c.; whence Co = 58·74. More recently (*ibid.* vii. 294), by dissolving metallic cobalt freed from oxide by strong ignition in a stream of hydrogen, in hydrochloric acid, measuring the quantity of hydrogen evolved, and reducing it to weight, Russell has found for the atomic weight of cobalt, Co = 58·76, a result which may be regarded as identical with the former. Sommaruga (*Pogg. Ann.* cxxx. 303; *Jahresb.* 1866, p. 244), by igniting cobaltous chloride in hydrogen, obtained the number 59·93, a result agreeing nearly with that which Schneider obtained (*Pogg. Ann.* ci. 387; *Jahresb.* 1857, p. 225) by determining the proportion of cobalt and carbon in pure cobaltous oxalate, viz. Co = 60·01. C. Winkler (*Zeitschr. anal. Chem.* vi. 18; *Jahresb.* 1867, p. 289) determines the atomic weight of cobalt by dissolving a known weight of the pure metal in excess of a neutral solution of auric chloride, and weighing the gold thereby separated; the reaction is expressed by the equation,

$$3Co + 2AuCl^3 = 3CoCl^2 + 2Au.$$

The mean of five experiments gave Co = 58·992. Hence Winkler concludes that the whole number 59 may be retained as the correct expression of the atomic weight of cobalt.

The following table exhibits all the values which have been given for the atomic weight of cobalt:

(1826) Rothoff	59·02	(1863) Russell	58·74
(1856) Marignac	58·64 59·02	(1867) Winkler	58·922
(1859) Dumas	59·08	(1869) Russell	58·78
(1857) Schneider	60·01	(1866) Sommaruga	59·93

Reactions of Cobalt Salts.—According to J. Bersch (*Zeitschr. f. Chem.* [2] iv. 308), the change of colour from red to blue which cobalt salts exhibit when heated, depends, not on difference of hydration, but on the formation of isomeric modifications. (See COBALT CHLORIDES, p. 476.)

1. A solution of a cobaltous salt mixed with 2 or 3 vol. strong *hydrochloric acid* acquires a blue colour of sufficient intensity to indicate the presence of $\frac{1}{20}$ milligrm. of cobalt in 1 c.c. of solution. Nickel and especially iron (but not manganese) interfere with the reaction, a small quantity of iron present in the cobalt solution changing the blue colour to emerald-green, while nickel changes the blue to green only when present in considerable quantity.

2. Cobalt nitrate mixed with a solution of acid sodium carbonate containing a small quantity of *hypochlorite*, forms a light green liquid of great colouring power, which, if not too concentrated, may be boiled for some hours without decomposition (Field, *Chem. Soc. Qu. J.* xiv. 78). A solution of a cobaltous salt mixed with acetate and hypochlorite of sodium, acquires a deep red colour, which on further addition of the hypochlorite, changes to a light yellow-brown. This mixture, even at ordinary temperatures, quickly becomes dark and almost black, but does not yield any precipitate, even when heated. On adding sodium carbonate and boiling, the whole of the cobalt is precipitated as peroxide, with deep brown colour. Any nickel that may be present also remains in solution until sodium carbonate is added (Popp, *Ann. Ch. Pharm.* cxxxi. 363).

3. If a cobaltous solution diluted till it no longer appears red be shaken up with a few crystals of *sodium pyrophosphate* till the latter are dissolved, and *sodium hypochlorite* be then added, a deep brown solution of cobaltic phosphate is produced, almost black if the solution is moderately concentrated. Nickel under the same circumstances forms a colourless liquid. This reaction may therefore serve to detect cobalt in presence of nickel; but care must be taken not to warm the solution, as in that case both metals would be precipitated as black hydrated peroxides (C. D. Braun, *Zeitschr. f. anal. Chem.* 1868, p. 348). According to Liebig, the nickel may be immediately recognised in another portion of the solution by adding potassium cyanide and excess of alkali, which produces a black colour due to nickel alone (*Zeitschr. f. Chem.* [2] v. 309).

4. When a cobaltous solution is mixed, first with a strong solution of *potassium cyanide* till the resulting precipitate is redissolved, then with a concentrated neutral solution of *potassium nitrite* and a few drops of acetic acid, the liquid immediately assumes a deep orange-red to blood-red colour, or, if somewhat dilute, an orange-rose colour (peach-blossom-red in thin layers), apparently due to the formation of potassio-cobaltous nitrocyanide, and disappearing on adding ammonia or excess of acid. This reaction is not exhibited by potassium-nickel cyanide, and may therefore serve as an additional test between cobalt and nickel; but the presence of nickel in the cobalt solution renders it less certain; moreover it is not so delicate as the well-known blowpipe reaction (C. D. Braun, *J. pr. Chem.* xci. 107).

5. A solution of cobaltous chloride acidulated with acetic acid gives with excess of *ammonium nitrite*, a yellow precipitate consisting of microscopic cubes, similar in appearance and analogous in composition to potassio-cobaltous nitrite (i. 1058) (Erdmann, *Jahresb.* 1866, p. 247). See NITRITES.

6. A solution of a cobaltous salt in tartaric or citric acid mixed with excess of ammonia and then with *potassium ferricyanide*, assumes a red colour, perceptible even in very dilute liquids (W. Skey, *Chem. News*, xv. 111).

7. An alkaline solution of *potassio-cobaltous cyanide* shaken up with air, assumes a deep brown-red colour (probably forming cobaltic cyanide), and after standing for some time, deposits part of the cobalt as cobaltic hydrate (not, however, in very dilute solutions), while potassium cobalticyanide remains dissolved. A nickel solution, under similar circumstances, neither forms a precipitate nor undergoes any change of colour (C. D. Braun, *Zeitschr. anal. Chem.* iii. 465).

8. *Cobalt sulphide* precipitated from an ammoniacal solution by yellow ammonium sulphide, and freed from excess of ammonia by heat, is less soluble in *potassium cyanide*, in proportion as the ammoniacal solution, before the addition of ammonium sulphide, has been longer exposed to the air, and therefore more completely converted into roseo-cobaltic or purpureo-cobaltic salt. The reaction affords the means of detecting cobalt in presence of nickel. If the precipitate formed by adding ammonium sulphide to the ammoniacal solution after exposure to the air, till it no longer changes colour, consists wholly of nickel sulphide, it will dissolve completely in potassium cyanide; but cobalt will remain undissolved as sesquisulphide, Co^2S^3; any small quantity of cobaltous sulphide, CoS, that may be present will impart to the solution in potassium cyanide a deep brown-red colour (H. Fleck, *ibid.* v. 399).

Quantitative Estimation.—Winkler (*Zeitschr. anal. Chem.* iii. 265, 420; *Jahresb.* 1864, p. 716; 1865, p. 723) has given a volumetric method of estimating cobalt in presence of nickel, based on the fact that on adding potassium permanganate to a solution of cobaltous chloride mixed with mercuric oxide, the whole of the cobalt is precipitated as cobaltic hydrate:

$$6CoCl^2 + 5HgO + Mn^2O^8K^2 + 5H^2O = 3(Co^2O^3.H^2O) + 2(MnO^2.H^2O) + 5HgCl^2 + 2KCl$$

The solution containing the cobalt and nickel (previously treated with barium chloride if it contains sulphuric acid) is mixed in the cold with precipitated and levigated mercuric oxide, and a normal solution of permanganate (titrated with pure cobalt solution) is gradually added, till the last drops give to the liquid a permanent amethyst colour. If the solution contains arsenic or phosphoric acid, these acids must be precipitated in the first instance by addition of ferric chloride. The excess of iron in the filtrate is then immediately precipitated as ferric oxide on adding the mercuric oxide, so that it does not interfere with the subsequent titration by the permanganate. The process gives exact results, provided the quantity of nickel present is not greater than twice that of the cobalt; in the contrary case it is best to precipitate the cobalt with potassium nitrite, mix the yellow precipitate with hydrochloric acid, evaporate to dryness, redissolve in water, and titrate the cobalt as above

(*Zeitschr. f. Chem.* [2] iv. 529). Terreil (*Bull. Soc. Chim.* [2] v. 88; *Jahresb.* 1866, p. 806) separates nickel and cobalt by means of ammonia and potassium permanganate, with subsequent addition of hydrochloric acid to the boiling solution, whereby the cobalt is precipitated as roseo-cobaltic chloride. According to Fresenius (*Zeitschr. anal. Chem.* v. 114), this method is not exact, because a small portion of the cobalt always escapes the oxidising action of the permanganate, and moreover the roseo-cobaltic chloride is not quite insoluble in water containing hydrochloric acid.

Cobalt and nickel may be separated from iron by boiling the solution of the nitrates for four hours with litharge, whereby the iron is precipitated as ferric oxide. The filtrate is freed from lead by hydrogen sulphide, and the cobalt and nickel determined by the usual methods (Field, *Chem. Centr.* 1860, p. 383).

From manganese the same metals may be separated by mixing the solution with ammonia and sal-ammoniac, and adding phosphoric acid, which throws down the manganese as ammonio-manganous phosphate, while the cobalt and nickel remain in solution* (S. H. Henry, *Phil. Mag.* [4] xvi. 197).

Cobalt Chloride. $CoCl^2$.—When a solution of this salt is concentrated till the boiling point rises to 111°, the remaining liquid, which solidifies on cooling to a red crystalline mass, has the composition $CoCl^2.6H^2O$; when further heated to 116° it is converted into $CoCl^2.4H^2O$. From this latter in the fused state blue crystals of the dihydrate $CoCl^2.2H^2O$ separate as the temperature rises, and at 121° the entire mass is converted into this hydrate, which does not give up the whole of its water till heated above 140°. The anhydrous chloride has a pale blue colour like that of recently precipitated cupric hydrate. When exposed to the air, it turns red in a few minutes, from absorption of water, and is converted, after some time, into the hydrate $CoCl^2.6H^2O$, without formation of the intermediate compounds; in contact with water, the same hydrate is quickly formed, and with considerable evolution of heat.

The *dihydrate* $CoCl^2.2H^2O$, prepared by heating either of the higher hydrates, forms a fused, deep violet-coloured, crystalline mass; when prepared by dehydrating the compound $CoCl^2.6H^2O$ over sulphuric acid, it forms a dark peach-blossom-coloured powder, which between 125° and 140° assumes the colour of sublimed chromic chloride. The dihydrate is extremely hygroscopic, and in contact with water is immediately converted into the hexhydrate.

The crystals of the *tetrahydrate* $CoCl^2.4H^2O$ have a peach-blossom-red colour; do not give off any water over sulphuric acid (unlike the hexhydrate), and when heated above 116° decrepitate without fusion, leaving the hydrate $CoCl^2.2H^2O$. When exposed to the air, they deliquesce to a solution from which the hexhydrate crystallises; in contact with water also they are converted into the same hydrate, with considerable increase of volume. It appears therefore that the dihydrate and tetrahydrate cannot exist in solution.

The currant-red crystals of the *hexhydrate*, $CoCl^2.6H^2O$, are permanent only in moist air; over sulphuric acid they quickly turn violet, and are ultimately converted into the dihydrate. On gently heating them, blue spots make their appearance at about 30° in the red crystalline mass, and continue to increase, till at 35° the entire mass has become blue without the slightest loss of weight; between 35° and 39° it swells up and splits into small spicular crystals which appear pale blue by reflected light, but are reconverted on cooling into the original red crystals. At 86°–87° they melt to an indigo-blue liquid, from which the red crystals do not separate till it is cooled to 50°. In water the hexhydrate dissolves very easily and with considerable lowering of temperature.

The changes of colour in the several hydrates take place without any diminution of weight, and appear to be due merely to molecular action. It appears probable, therefore, that the chloride and other analogous compounds of cobalt (which exhibit similar changes of colour) are susceptible of two modifications, a red and a blue, and that the latter can exist in the tetra- and hex-hydrated chlorides only at comparatively high temperatures, but that in the dihydrate it can exist also at ordinary temperatures; moreover, all cobaltous compounds turn blue when heated, quite independently of any change in their amount of water (J. Bersch, *Wien. Akad. Ber.* lvi. [2] 724; *Jahresb.* 1867, p. 291).

Oxides. *Hydrated cobaltoso-cobaltic oxide*, $2Co^3O^4.H^2O$, is obtained by heating the commercial basic carbonate, $2CoCO^3.CoH^2O^2 + 3aq.$, to 200° for twelve hours. [H. Rose (*Pogg. Ann.* lxxxiv. 553) regarded the product thus obtained as hydrated cobaltic oxide, $4Co^2O^3.H^2O$.] This hydrate exposed to the air gradually takes up water and is converted into the *dihydrate* $Co^3O^4.2H^2O$. The latter dried at 100°

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* According to Chancel, on the other hand, cobalt and nickel are completely precipitated by phosphoric acid from *cold* ammoniacal solutions (*Jahresb.* 1866, p. 805).

leaves the hydrate $4Co^3O^4.5H^2O$, and at 110°, the hydrate $4Co^3O^4.3H^2O$. Any oxide of cobalt ignited for about a quarter of an hour in a half-covered crucible over an ordinary gas-flame, and then quickly cooled, is converted into cobaltoso-cobaltic oxide, Co^3O^4; but if the ignition be performed over a gas-flame urged by a blast, the residue consists chiefly of cobaltous oxide, CoO (C. D. Braun, *Zeitschr. anal. Chem.* vi. 76). According to Russell (*Chem. Soc. J.* [2] i. 51), cobaltoso-cobaltic oxide ignited over the gas blowpipe flame in an atmosphere of carbon dioxide, leaves pure cobaltous oxide.

Cobaltic Acid (?).—According to Winkler (*J. pr. Chem.* xci. 213; *Jahresb.* 1864, p. 267), finely divided (reduced) cobalt dissolves when boiled for a long time with its own weight of potassium hydrate and 3 pts. water, forming a deep blue liquid in which the cobalt exists as CoO^3. The potassium-cobaltate has not been isolated in the solid state, and the solution itself decomposes spontaneously, losing its blue colour; chlorine passed into it gives rise to a rapid emission of oxygen. Winkler analysed it by determining the quantity of sulphuric acid formed by treating a known quantity with sulphurous acid. According to Schultze, however, Winkler's cobaltate is nothing but an alkaline solution of cobaltic hydrate (*Jahresb.* 1864, p. 269).

COBALT BASES, AMMONIACAL (i. 1051). The general formulæ of the several ammonio-cobaltic compounds, according to the atomic weight of cobalt now admitted [Co = 59], are represented in the following table, in which X denotes an atom of chlorine or of an equivalent acid radicle such as NO^2, $C^2H^3O^2$, $\frac{1}{2}(SO^4)$, &c.:

Tetrammonio-cobaltic salts	$Co^2X^6.4NH^3$
Hexammonio-cobaltic salts	$Co^2X^6.6NH^3$
Oxy-octammonio-cobaltic (fusco-cobaltic) salts . .	$Co^2OX^4.8NH^3$
Decammonio-cobaltic (roseo- and purpureo-cobaltic) salts	$Co^2X^6.10NH^3$
Dinitro-decammonio-cobaltic (xantho-cobaltic) salts .	$Co^2(NO^2)^2X^4.10NH^3$
Dodecammonio-cobaltic (luteo-cobaltic) salts . .	$Co^2X^6.12NH^3$
Oxy-cobaltic salts	$CoOX^2.5NH^3$

Many of these salts have been further examined by Braun (*Ann. Ch. Pharm.* cxxxii. 33; cxlii. 50; *Jahresb.* 1864, p. 270; 1867, p. 294).

Fusco-cobaltic salts are easily resolved under the influence of ammonia and of acids into roseo- and luteo-cobaltic salts; thus when fusco-cobaltic chloride is heated with concentrated hydrochloric acid, roseo-cobaltic chloride, which is the principal product, is always mixed with a certain quantity of luteo-cobaltic salt:

$$4(\underset{\text{Fusco.}}{Co^2OCl^4.8NH^3}) + 2HCl = 2(\underset{\text{Roseo.}}{Co^2Cl^6.10NH^3}) + \underset{\text{Luteo.}}{Co^2Cl^6.12NH^3} + Co^2O^3 + H^2O.$$

With dilute hydrochloric acid, on the other hand, the luteo-cobaltic chloride predominates; thus:

$$10(\underset{\text{Fusco.}}{Co^2OCl^4.8NH^3}) + 2HCl = 2(\underset{\text{Roseo.}}{Co^2Cl^6.10NH^3}) + 5(\underset{\text{Luteo.}}{Co^2Cl^6.12NH^3}) + 3Co^2O^3 + H^2O.$$

Roseo-cobaltic chloride may be prepared synthetically from fusco- and luteo-cobaltic chlorides. When these two chlorides are heated together with ammonia for several days in a sealed tube, placed in a sand-bath, there is obtained, together with undecomposed fusco-cobaltic salt and cobaltic hydrate, a red liquid from which roseo-cobaltic chloride gradually crystallises:

$$3(\underset{\substack{\text{Fusco-cobaltic}\\\text{chloride.}}}{Co^2OCl^4.8NH^3}) + 2(\underset{\substack{\text{Luteo-cobaltic}\\\text{chloride.}}}{Co^2Cl^6.12NH^3}) + 2NH^3 = 4(\underset{\substack{\text{Roseo-cobaltic}\\\text{chloride.}}}{Co^2Cl^6.10NH^3}) + \underset{\substack{\text{Roseo-cobaltic}\\\text{oxide.}}}{Co^2O^3.10NH^3}$$

The separated cobaltic oxide arises from the decomposition of the free roseo-cobaltic oxide.

Roseo-cobaltic chloride is also produced by agitating a moderately concentrated solution of cobaltous nitrate with strong aqueous ammonia till it appears clear and of a dark brown colour, and then heating it for half an hour to an hour with pure indigo-blue; the liquid then assumes a deep violet-red colour, gradually changing to wine-red on exposure to the air, and on addition of strong hydrochloric acid deposits after a while microscopic tetragonal crystals of roseo-cobaltic chloride. The reaction may be represented by the equation:

$$\underset{\text{Indigo-blue.}}{2C^8H^5NO} + H^2O + 2CoO + 10NH^3 = \underset{\substack{\text{Roseo-cobaltic}\\\text{oxide.}}}{Co^2O^3.10NH^3} + \underset{\text{Indigo-white.}}{C^{16}H^{12}N^2O^2}$$

Roseo-cobaltic Sulphate. $Co^2(SO^4)^3.10NH^3 + 5aq.$ (i. 1053).—According to Braun (*Ann. Ch. Pharm.* cxxxviii. 109), the oxidised ammoniacal solution of ammonio-cobaltous sulphate is not precipitated by sulphuric acid till after the addition of water or alcohol. The precipitated pulverulent salt gives off 5 mol. water at 100°, without losing its solubility, which is moderately great even in cold water. The salt decomposed with baryta-water yields roseo-cobaltic oxide, the strongly alkaline solution of which absorbs carbonic acid from the air.

Xantho-cobaltic Salts. $CoOX^4.10NH^3.2NO.H^2O$ according to Gibbs a. Genth (i. 1054), $Co(NO^2)^2X^4.10NH^3$ according to Braun.—These formulæ differ from one another only by H^2, a difference not recognisable by analysis. Braun's formula is verified by the decomposition of the chloride with ferrous salts, the oxygen which it gives up to a titrated ferrous solution being estimated volumetrically. These salts digested in dilute solution for several days at a gentle heat with strong aqueous ammonia, are converted into roseo- and luteo-cobaltic salts, with separation of nitrous acid. When a small quantity of xantho-cobaltic nitrate is warmed with aqueous ammonia, a strong solution of sodium-pyrophosphate added, and the liquid again warmed, crystalline laminæ of luteo-cobaltic pyrophosphate are quickly produced. A strong solution of xantho-cobaltic nitrate and an equal quantity of sal-ammoniac heated with strong hydrochloric acid, yield the chlorides of roseo- and luteo-cobaltic chlorides, according to the equation:

$$\underset{\text{Xantho-cobaltic nitrate.}}{2[Co^2(NO^2)^2(NO^3)^4.10NH^3]} + 10HCl + 2NH^4Cl = \underset{\substack{\text{Roseo-cobaltic}\\ \text{chloride.}}}{Co^2Cl^6.10NH^3} +$$

$$\underset{\substack{\text{Luteo-cobaltic}\\ \text{chloride.}}}{Co^2Cl^6.12NH^3} + \underset{\substack{\text{Nitrous}\\ \text{acid.}}}{4NO^2H} + \underset{\substack{\text{Nitric}\\ \text{oxide.}}}{8NO^3H}$$

If dilute hydrochloric acid (sp. gr. 1·12) be used, and the temperature kept at about 60°, the chief product is luteo-cobaltic chloride. A mixture of the concentrated solutions of xantho-cobaltic nitrate and ammonium sulphate heated with hydrochloric acid, or of xantho-cobaltic nitrate and ammonium chloride heated with sulphuric acid, yields luteo-cobaltic sulphate and chloride, generally with a small quantity of roseo-cobaltic salt.

Luteo-cobaltic chloride may also be prepared by agitating a solution of cobaltous chloride or nitrate with strong aqueous ammonia and lumps of sal-ammoniac, adding lead dioxide to the dark brown liquid, and keeping the mixture in gentle ebullition for about half an hour. With sufficient oxidation and abundant addition of sal-ammoniac, the dark reddish-yellow liquid contains chiefly luteo-cobaltic chloride, together with a very small quantity of roseo-cobaltic chloride; with a smaller quantity of sal-ammoniac, the latter is more abundantly produced. Hydrochloric acid separates the luteo-cobaltic chloride from the concentrated liquid, as a yellow crystalline powder; from a dilute solution after a day or two, in needle-shaped crystals (Braun).

Mills (*Phil. Mag.* [4] xxxv. 245) prepares *luteo-cobaltic chloride* by heating cobaltous chloride with sal-ammoniac, aqueous ammonia, and a powerful oxidising agent under pressure (in a soda-water bottle closed with a caoutchouc stopper) to 70° for about twenty hours. Equal weights (15 grms.) of cobalt chloride, sal-ammoniac, and potassium permanganate heated in this manner with six times the weight of strong aqueous ammonia, form an orange-yellow liquid, together with nodular aggregations of luteo-cobaltic chloride and a copious precipitate of the higher oxides of manganese and cobalt. The liquid is poured into excess of hydrochloric acid; the crystals are dissolved in water acidulated with hydrochloric acid; these solutions are mixed; the resulting liquid, together with twice its volume of strong aqueous hydrochloric acid, is left to itself for 24 hours; and the yellow precipitate of luteo-cobaltic chloride thereby separated is washed on a filter with hydrochloric acid, and finally with alcohol: it amounts to 71 p. c. of the theoretical quantity. If the permanganate is replaced in the preparation by an equal weight of dichromate, the product amounts to nearly 80 p. c. Manganese dioxide, cobaltic oxide, iodine, or bromine may also be used as the oxidising agent. Cobaltic oxide treated as above with a large quantity of sal-ammoniac and strong ammonia is almost wholly converted into luteo-cobaltic chloride. Mixtures of cobaltous chloride and sal-ammoniac with ammonia and solid chloride of lime also yield a yellow precipitate after long standing in contact with hydrochloric acid. On the other hand, purpureo-cobaltic chloride boiled with aqueous ammonia yields but a very small quantity of luteo-cobaltic chloride. Purpureo-cobaltic chloride is not altered in weight when heated to 87° with ammonia; hence, and from certain weight-determinations, Mills concludes that the formation of luteo-cobaltic chloride from purpureo-cobaltic chloride does not depend upon a simple addition of ammonia. Moreover, when purpureo-cobaltic chloride is heated with water and ethylamine, aniline, or pyridine (instead of ammonia), only ordinary luteo-cobaltic chloride is formed (besides the other products of decomposition): whence it appears that the luteo-cobaltic chloride is formed at the expense, not of the free ammonia, but of ammonia eliminated from the purpureo-cobaltic chloride.

To prepare *purpureo-cobaltic chloride*, 5 pts. of crystallised cobaltous chloride and 5 pts. sal-ammoniac are dissolved in 100 pts. of water; the cooled solution is mixed with 22 pts. strong aqueous ammonia and 2 pts. chloride of lime; and the mixture, after exposure to the air for 24 hours, is boiled with a large excess of hydrochloric acid, and left to crystallise.

Roseo-cobaltic chloride may be obtained quite pure by mixing an aqueous solution of 5 grms. crystallised cobaltous chloride diluted to 90 c.c. with 27·5 c.c. strong ammonia and 2·5 grms. potassium permanganate dissolved in 100 c.c. water, the temperature of the liquids before mixing not being allowed to rise above 18°. The solution after 24 hours' exposure to the air is filtered from the manganese precipitate; neutralised with dilute hydrochloric acid; precipitated with a cold mixture of 3 vol. hydrochloric acid and ½ vol. alcohol; and the salt is washed first with the same mixture, then with alcohol alone. The product thus obtained has the composition $10NH^3.Co^2Cl^6 + H^2O$; it is quite free from purpureo-cobaltic chloride, but is immediately converted into that salt on heating its solution with a trace of hydrochloric acid. The solution of pure roseo-cobaltic chloride is not precipitated by potassium iodide or neutral potassium chromate; with the dichromate it forms a brick-red precipitate.

Luteo-cobaltic chloride heated with water to 70°–80° in sealed tubes is easily decomposed, forming a colourless solution of cobaltous chloride, ammonia, and sal-ammoniac, with a trace of nitric acid, and a black precipitate having nearly the composition of the oxide Co^4O^5, mixed with silica arising from decomposition of the glass. Purpureo-cobaltic chloride is decomposed by water in a similar manner, but less quickly and completely, on account of its smaller solubility in ammoniacal sal-ammoniac. These decompositions appear to take place by two stages, part of the compound being first resolved into cobaltous chloride, free chlorine, and ammonia (which react with the water so as to form nitrogen, ammonium chloride, and a little nitric acid), and the cobaltous chloride exerts a further decomposing action on the remaining portion of the original compound:

For Purpureo-cobaltic chloride:

$$\text{I. } a. \quad Co^2Cl^6.10NH^3 = 2CoCl^2 + 10NH^3 + Cl^2.$$
$$\text{II. } a. \quad Co^2Cl^6.10NH^3 + 2CoCl^2 + (5+n)H^2O = Co^4O^5.nH^2O + 10NH^4Cl.$$

For Luteo-cobaltic chloride:

$$\text{I. } b. \quad Co^2Cl^6.12NH^3 = 2CoCl^2 + 12NH^3 + Cl^2.$$
$$\text{II. } b. \quad Co^2Cl^6.12NH^3 + 2CoCl^2 + (5+n)H^2O = Co^4O^5.nH^2O + 10NH^4Cl + 2NH^3.$$

Both these cobalt-ammonium chlorides are in fact decomposed by heating with cobaltous chloride and water, forming precipitates which always contain less oxygen than Co^2O^3, but (probably in consequence of subsequent oxidation) more than Co^4O^5 or Co^5O^6. The conditions under which the liquid remains neutral are given for purpureo-cobaltic chloride by the equation II. *a*; for luteo-cobaltic chloride by the equation:

$$Co^2Cl^6.12NH^3 + 3CoCl^2 + (6+n)H^2O = Co^5O^6.nH^2O + 12NH^4Cl.$$

The strong corrosion of the glass which takes place when these chlorides are heated with ammonia and water is attributed by Mills to the transient formation of the hydrates $Co^2Cl^{6-2n}(HO)^{2n}.10NH^3$ and $Co^2Cl^{6-2n}(HO)^{2n}.12NH^3$. Aqueous ammonia does not act upon glass when heated in it either alone or with the precipitates; cobaltic oxide with sal-ammoniac solution (which produces cobaltous chloride) acts but slightly.

For the further development of Schiff's views on the constitution of the ammoniacal cobalt-compounds, see *Ann. Ch. Pharm.* cxxiii. 1; *Rép. Chim. pure*, iv. 380; *Jahresb.* 1862, p. 198. Respecting the salts which Geuther obtained by the action of ammonium sulphite on cobaltic hydrate, see SULPHITES (v. 544).

COCAINE (i. 1059). W. Lossen (*Ann. Ch. Pharm.* cxxxiii. 351) purifies this base by dialysing the solution of the crude hydrochloride, precipitating the solution thus freed from colouring matter with sodium carbonate, and repeatedly crystallising the precipitated base from alcohol. Lossen assigns to cocaine the formula $C^{17}H^{21}NO^4$, which likewise agrees with Niemann's analyses. According to Tchermak

(*Wien. Akad. Ber.* xlviii. [i] 34), the crystals of cocaine are monoclinic, exhibiting the combination oP . ∞P∞ . −P . −P∞ . (P∞), the inciined axes *b*, *c* forming an angle of 73° 50′, and the ratio of the axes *a* : *b* : *c* being equal to 1·186 : 1 : 1·223. Angle oP : −P∞ = 119° 20′; oP : (P∞) = 135° 16′; −P : oP = 11·3° 14′. The crystals are prismatically elongated in the direction of the orthodiagonal, mostly hemimorphously developed in this direction, and imperfectly cleavable parallel to oP.

Cocaine dissolves easily in dilute acids, forming mostly crystallisable salts which are soluble in alcohol, but not in ether, have a bitter taste, and, like the free base, produce a transient numbing sensation on the tongue. The *hydrochloride* $C^{17}H^{21}NO^4.HCl$ crystallises from alcohol in short prisms, perpendicularly truncated at the ends; the *platinochloride* $2(C^{17}H^{21}NO^4.HCl).PtCl^4$ and the *aurochloride* $C^{17}H^{21}NO^4.HCl.AuCl^3$ are light yellow precipitates. The *sulphate* is gummy, and crystallises but slowly; the *neutral oxalate* crystallises quickly; an *acid oxalate*, $C^{17}H^{21}NO^4.C^2H^2O^4$, is deposited in feathery crystals on adding ether to an alcoholic solution of dehydrated oxalic acid and cocaine. The solution of cocaine in acetic acid leaves the pure base on evaporation (Lossen).

Cocaine heated with strong hydrochloric acid is resolved into ecgonine (*q.v.*), benzoic acid, and methyl alcohol (Lossen):

$$\underset{\text{Cocaine.}}{C^{17}H^{21}NO^4} + 2H^2O = \underset{\text{Ecgonine.}}{C^9H^{15}NO^3} + \underset{\text{Benzoic acid.}}{C^7H^6O^2} + \underset{\text{Methyl alcohol.}}{CH^4O}$$

COCCININ. See CARMINIC ACID (p. 414).

COCHINEAL. The ash of silver-grey Honduras cochineal, amounting to 3·2 p. c., contains in 100 pts.: 18·63 K^2O, 13·40 Na^2O, 0·51 NaCl, 2·40 CaO, 16·44 MgO, 1·39 Al^2O^3, 1·15 Fe^2O^3, 47·25 P^2O^5, and 7·92 SiO^2 (E. Dieterich, *Chem. Centr.* 1867, p. 287).

Cochineal-wax.—A species of cochineal (*Coccus Caricæ*, Fabr.; *Columnea testudiformis*, Tozzetto) living on the fig-trees of Italy, contains a wax differing from beeswax only in the proportion of its constituents. Ether extracts from the insects about 65 p. c. of this wax, which is red-brown, melts at 51° to 52°, dissolves but partially in alcohol, and contains 51·3 p. c. ceroleïn, 12·7 cerotic acid, and 35·2 myricin, with very small quantities of butyric and valeric acids. The wax (about 59 p. c.) expressed from the cochineal under boiling water is grey after remelting, and melts at 57°; when freed from the greater part of the ceroleïn by alcohol it melts at 62° to 63°, and when bleached resembles ordinary beeswax (F. Sestini, *Bull. Soc. Chim.* [2] vii. 482).

CODAMINE. $C^{19}H^{23}NO^3$.—A base recently obtained, together with others, by Hesse (*Ann. Ch. Pharm.* cliii. 47), from the aqueous extract of opium. When recrystallised from ether, it forms large colourless six-sided prisms, mostly terminated by domes; soluble in alcohol, ether, and boiling water; very soluble in chloroform and benzol. All these solutions have an alkaline reaction, neutralise acids, and form salts which have a bitter taste and are mostly amorphous. The base melts at 121°, solidifies to an amorphous mass on cooling, decomposes at a higher temperature. It dissolves in strong nitric acid with dark green, in strong sulphuric acid with blue colour, changing to green, and afterwards to dark violet on warming the liquid. Ammonia and potash produce in solutions of the salts a white flocculent precipitate soluble in excess. The *platinochloride* $2(C^{19}H^{23}NO^3.HCl).PtCl^4$ is a yellow amorphous precipitate slightly soluble in water and in hydrochloric acid.

CODEINE. $C^{18}H^{21}NO^3$.—The action of hydrochloric acid on this base has recently been studied by Matthiessen a. Wright (*Proc. Roy. Soc.* xvii. 460; xviii. 83). Codeine heated with excess of hydrochloric acid in sealed tubes splits up into methyl chloride, water, and apomorphine (see MORPHINE):

$$C^{18}H^{21}NO^3 + HCl = CH^3Cl + H^2O + C^{17}H^{17}NO^2.$$

But when the reaction takes place under the ordinary atmospheric pressure, and at the temperature of the water-bath, a chlorinated base called chlorocodide is produced derived from codeine by substitution of Cl for HO; thus:

$$\underset{\text{Codeine.}}{C^{18}H^{20}(HO)NO^2} + HCl = H(HO) + \underset{\text{Chlorocodide.}}{C^{18}H^{20}ClNO^2}$$

To obtain this base in the pure state, codeine is heated under paraffin on the water-bath with 10 to 15 times its weight of strong hydrochloric acid for 12 to 15 hours; the resulting brownish liquid is evaporated to dryness; and the residue dissolved in water is mixed with sodium bicarbonate, whereby a bulky white precipitate is formed consisting chiefly of chlorocodide, with a trace of apomorphine. This precipitate, freed from the apomorphine by washing with dilute ammonia, is dissolved in hydrochloric acid and fractionally precipitated with sodium bicarbonate; and the second fraction, which is pure white and free from codeine and apomorphine, is exhausted with ether, which dissolves nearly the whole. The clear ethereal solution is then shaken up with a few drops of hydrochloric acid, and the resulting solution of hydrochloride is fractionally precipitated with sodium bicarbonate, and the treatment with ether and hydrochloric acid is repeated. The product is a viscid colourless solution of the pure hydrochloride, which refuses to crystallise. By fractional precipitation with sodium bicarbonate it yields pure chlorocodide as a snow-white mass, scarcely affected by exposure to air, very soluble in alcohol and ether, but not crystallisable therefrom, owing to decomposition. Its physiological action is much less marked than that of apomorphine, doses of $\frac{1}{4}$ grain taken internally and $\frac{1}{10}$ gr. injected subcutaneously producing no appreciable effect. The *hydrochloride* contains $C^{18}H^{20}ClNO^2.HCl$; the *platinochloride* $2(C^{18}H^{20}ClNO^2.HCl).PtCl^4$ is a yellow precipitate permanent in the air, but decomposing in the moist state at 100°.

A solution of the hydrochloride of chlorocodide gives a pale amethyst coloration with *ferric chloride*; pale red with *nitric acid*; evanescent pale red with *sulphuric acid* and *potassium dichromate*; pale red with solution of *bleaching powder* and a drop of hydrochloric acid; a white precipitate with *corrosive sublimate*, decomposing with pale red colour on boiling; it reduces *silver* from the nitrate; gives with *caustic potash, ammonia*, and *sodium carbonate*, white precipitates slightly soluble in excess; white precipitates also with *potassium iodide and sodium phosphate.**

When the hydrochloride is heated to 140°–150° for three hours with 8 to 15 times its weight of strong *hydrochloric acid*, the base is resolved into methyl chloride and apomorphine:

$$C^{18}H^{20}ClNO^2 = CH^3Cl + C^{17}H^{17}NO^2.$$

The hydrochloride heated in a similar manner with 10 to 15 times its weight of *water*, splits up into hydrochloric acid and codeine hydrochloride without any evolution of gas:

$$C^{18}H^{20}ClNO^2.HCl + H(HO) = HCl + C^{18}H^{20}(HO)NO^2.HCl.$$

This reaction is the inverse of that which takes place when codeine is heated on the water-bath with excess of hydrochloric acid.

Codeine heated with *hydrobromic acid* is converted, in the first instance, into bromocodide, $C^{18}H^{20}BrNO^2$, analogous to chlorocodide; and this by further heating with codeine is converted into deoxycodeine and bromotetracodeine:

$$\underset{\text{Bromocodide.}}{C^{18}H^{20}BrNO^2} + \underset{\text{Codeine.}}{4C^{18}H^{21}NO^3} = \underset{\text{Deoxycodeine.}}{C^{18}H^{21}NO^2} + \underset{\text{Bromotetracodeine.}}{C^{72}H^{83}BrN^4O^{12}}$$

(Wright, *Proc. Roy. Soc.* xix. 371.)

Codeine heated with *hydriodic acid* yields the hydriodide of a new base not yet examined (Matthiessen a. Burnside).

Apocodeine or **Apocodeia.** $C^{18}H^{19}NO^2$ (Matthiessen a. Burnside, *Proc. Roy. Soc.* xix. 71).—This base, containing the elements of 1 mol. H^2O less than codeine, is produced by heating codeine hydrochloride with a concentrated solution of zinc chloride to 170°–180° for about fifteen minutes. On cooling, a yellowish-brown tarry mass separates from the liquid, which on further cooling may be drawn out into threads, and thus obtained almost free from zinc chloride. It consists of almost pure apocodeine hydrochloride, and may be further purified by repeated solution in hot water and precipitation with hydrochloric acid. By dissolving this salt in water, precipitating with sodium carbonate, exhausting with ether, and evaporating, apocodeine is obtained as an amorphous, gummy, reddish mass, soluble in alcohol, ether, and chloroform, insoluble in water, and uncrystallisable. It is much more stable than apomorphine, and therefore more easily prepared. Its reactions are nearly identical with those of apomorphine (see MORPHINE), the chief difference being that the blood-red colour which apocodeine gives with nitric acid is much more permanent than that obtained with apomorphine. *Hydrochloride* of *apocodeine* is amorphous, whereas the apomorphine salt is crystalline. The apocodeine salt is a mild emetic, whereas apomorphine hydrochloride acts as a very violent emetic. The apocodeine salt produces subcutaneous abscesses at the point of injection, which the apomorphine salt does not.

Codeine heated with sulphuric acid (equal volumes of hydrogen sulphate and water) is converted, first into an amorphous base having the same composition; then, by abstraction of $\frac{1}{2}$ mol. water, into a base intermediate between codeine and apocodeine: $2C^{18}H^{21}NO^3 - H^2O = C^{36}H^{40}N^2O^5$; then into apocodeine, which lastly undergoes further change, apparently into apomorphine, by removal of CH^3 (Armstrong, *Chem. Soc. J.* [2] ix. 59).

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* The behaviour of codeine to the above reagents is nearly the same as that of morphine (*q.v.*).

CŒRULEÏN. A blue colouring matter existing in certain volatile oils obtained from plants, chiefly of the composite order. (See Oils, iv. 185.)

COLCHICINE (i. 1080). This alkaloïd has been further examined by Hübler (*Chem. Centr.* 1865, p. 536; *Jahresb.* 1864, p. 450), who assigns to it the formula $C^{17}H^{19}NO^5$ and regards it as isomeric with colchiceine. He prepares it by exhausting colchicum-seeds with boiling alcohol; diluting the filtered solution with at least 20 times its volume of water, which separates a fatty oil; treating the decanted watery liquid with basic lead acetate to remove colouring matters; and precipitating the excess of lead with sodium phosphate. The solution thus freed from foreign substances is fractionally precipitated with a solution of tannin, which throws down a compound of 3 mol. colchicine and 1 mol. tannic acid. The middle portion of this precipitate, which is the least coloured, is further purified by pressure and washing with a small quantity of water; then mixed with excess of levigated litharge and dried; the colchicine is extracted from the residue by alcohol; and the evaporated extract is again subjected to fractional precipitation with tannin and treatment with litharge, till the product exhibits a pure sulphur-yellow colour and dissolves completely in water and in alcohol.

Colchicine thus obtained is an amorphous substance having a faint aromatic odour and intensely bitter taste. It melts at 140°, is insoluble in ether, but easily soluble in water and in alcohol, neutral to litmus-paper; forms a yellow precipitate with auric chloride, white with mercuric chloride, and a curdy precipitate with tannic acid. Alkalis and strong mineral acids colour its solution deep yellow.

Colchiceine, produced by the action of dilute sulphuric acid, alkalis, or baryta-water on colchicine, has, according to Hübner, the same composition as the latter. By repeated crystallisation from water, and finally from alcohol, it may be obtained in nodular groups of colourless needles which are much less bitter than colchicine, and are soluble in chloroform, less soluble in ether. It is completely abstracted from its aqueous solution by animal charcoal, being converted at the same time into a brown uncrystallisable substance, which is also easily formed from colchiceine on exposure to the air. Colchiceine has an acid reaction, dissolves easily in alkalis (in carbonates with evolution of carbon dioxide), forming amorphous salts whose solutions are precipitated by solutions of the alkaline earths and heavy metals; the copper-compound is crystallisable; the amorphous barium-compound has nearly the composition $(C^{17}H^{18}NO^5)^2Ba$.

COLLOÏDAL ACIDS. See Appendix, v. 1088.

COLOPHONIN. $C^{10}H^{22}O^3$ (C. Tichborne, *Chem. News*, xx. 38).—When old *esscnce of resin* (obtained by distillation of colophony, i. 1087) is washed with water and the wash-water is evaporated, colophonin hydrate, $C^{10}H^{22}O^3.H^2O$, is obtained in large well-defined crystals having a sweet taste, destitute of odour, easily soluble in water, alcohol, ether, chloroform, and carbon bisulphide, less soluble in benzol and in essence of resin; from water it crystallises in fine colourless prisms. When heated it melts and sublimes, with partial loss of water. It also gives off water and effloresces when left over sulphuric acid. It may be completely dehydrated by prolonged fusion in a test-tube, the water which condenses in the upper part of the tube being continually removed by bibulous paper, and the sublimed crystals continually pushed back into the fused mass till no more water is given off. The compound thus dehydrated gave by analysis numbers agreeing with the formula $C^{10}H^{22}O^3$. Anhydrous colophonin and its hydrate differ from terpin and terpin hydrate respectively, by containing the elements of 1 mol. H^2O in addition. *Bromine* acts very strongly on colophonin hydrate, with formation of hydrobromic acid and separation of carbon. On the aqueous solution it acts less violently, forming an oil which appears to be a tetrabrominated substitution-product. The solution of the hydrate is optically inactive. When heated with *acids* (sulphuric, phosphoric, arsenic, citric, and tartaric), and then with alcohol, it exhibits a green colour; with most acids it is necessary to apply heat, but with sulphuric acid the reaction takes place in the cold. Under certain circumstances the green colour is also produced by hydrochloric acid; but when the hydrate is treated with strong hydrochloric acid, and the mass after half an hour is shaken up with alcohol, a fine rose colour is developed. If the hydrochloric acid be allowed to act for a longer time, various shades of violet are produced, and ultimately a fine pure indigo-blue. None of these reactions are exhibited by terpin hydrate.

COLOPHONY. See Sylvic Acid.

COMBUSTION. 1. *Temperature of Flame.*—Experiments on the temperatures of the flames of carbon monoxide and hydrogen have been made by Bunsen (*Pogg. Ann.* cxxxi. 161; *Phil. Mag.* [4] xxxiv. 489; *Jahresb.* 1867, 39). When a combustible gas mixed with oxygen is set on fire, a rise of temperature takes place, which, supposing the combustion to be perfect, may be calculated from the heat of combustion of the gases and the specific heat of the products. If on the other hand the combustion is imperfect, the temperature may still be calculated, with the aid of Mariotte's and Gay-Lussac's laws, provided the pressure be known which is exerted by the gaseous mixture when exploded in a closed vessel. This pressure has been determined by Bunsen in the case of mixtures of hydrogen or carbon monoxide with oxygen, or with oxygen and nitrogen together, by means of a eudiometer provided with a loaded safety valve. From this and the observed temperature of combustion, the quantity of the combustible gas (CO or H) which has been burnt at the moment when the flame attains its maximum temperature, and thence also the quantity which at this temperature has lost its power of combining, may be calculated.

The following table contains the results of the experiments, arranged according to the maxima of temperature, $t'-t$, which the several gaseous mixtures, calculated for volumes at 0°, attain by combustion in a closed vessel. Column III. gives the maximum temperatures for the mixtures in columns I. and II.; column IV. shows the fraction of the gas (CO or H) which has been burned:

I.	II.	III.	IV.	Mean	Deviation from the mean
⅔ vol. CO ⅓ „ O	0·0000 vol.	3172°	0·351		+ 0·0194
⅔ „ CO ⅓ „ O	0·0000 „	2893	0·319		− 0·0126
⅔ „ H ⅓ „ O	0·0000 „	2854	0·338	0·3316	+ 0·0064
⅔ „ H ⅓ „ O	0·0000 „	2833	0·336		+ 0·0044
⅔ „ CO ⅓ „ O	0·1079 „ O	2558	0·314		− 0·0176
⅔ „ CO ⅓ „ O	0·6857 „ CO	2471	0·460		− 0·0421
⅔ „ CO ⅓ „ O	0·8854 „ O	2325	0·478		− 0·0241
⅔ „ CO ⅓ „ O	1·0861 „ O	2117	0·490		− 0·0121
⅔ „ CO ⅓ „ O	1·2563 „ N	2084	0·515		+ 0·0129
⅔ „ H ⅓ „ O	1·2599 „ N	2024	0·547	0·5021	+ 0·0449
⅔ „ CO ⅓ „ O	1·2563 „ N	1909	0·470		− 0·0321
⅔ „ CO ⅓ „ O	1·7145 „ O	1726	0·520		+ 0·0179
⅔ „ CO ⅓ „ O	2·1559 „ O	1460	0·512		+ 0·0099
⅔ „ CO ⅓ „ O	3·1629 „ CO	1146	0·527		+ 0·0249

These numbers show that in a mixture of carbon monoxide or hydrogen with the exact proportion of oxygen required for combination, and unmixed with any indifferent gas, only one-third of the carbon monoxide or hydrogen is burnt at the maximum temperature, whilst the other two-thirds, by being raised to the high temperatures of 2558°–3033°, have lost the power of combining; moreover, that when 1 vol. of the same mixtures is diluted with 0·686 to 3163 vol. of any gas that does not burn with it, and the temperature of the flame is thereby successively reduced from 2471° to 1146°, then, at all temperatures within this range, almost exactly half of the carbon monoxide or hydrogen is burnt, whilst in the other half, the oxygen and carbon monoxide, or the oxygen and hydrogen, have lost the power of combining.

The combustion of gases appears therefore to take place in a manner very different from that which has been hitherto supposed. When a mixture of 2 vol. carbon monoxide and 1 vol. oxygen is set on fire, and its temperature thereby raised from 0° to 3033°, two-thirds of the carbon monoxide present remains in the unburnt and incombustible state; the temperature is then lowered, by radiation and conduction, from 3033° to 2558° without any combustion of this two-thirds of the carbon monoxide; but when the temperature falls somewhat lower, combustion recommences, restoring the heat lost by radiation and conduction, and raising the temperature again to 2558°, but not above that point. The gradual fall of temperature from 3033° is followed by a continuance of the temperature of 2558° till exactly half of the carbon monoxide is burnt, whereupon a third phase sets in, during which again no combustion takes place till the inflamed gaseous mixture has cooled down to at least 1146°. As, however, the gaseous mixture, after cooling, consists almost wholly of carbon dioxide, these alternate phases of constant and decreasing temperature must likewise be repeated below 1146°, till the last portion of gas is burnt. This discontinuous combustion of a uniform mixture of a combustible gas with oxygen is referred by Bunsen to a law of combination which he established some years ago. (See CHEMICAL AFFINITY, i. 860.)

In connection with this investigation, Bunsen has determined, by special experiments, the rate of propagation of the combustion in a pure detonating mixture of hydrogen and oxygen, and likewise of carbon monoxide and oxygen; in the former he finds the velocity of propagation to be 34 metres per second; in the latter less than 1 metre per second. When the explosive gaseous mixtures are gradually more and more diluted with a gas which does not take part in the combustion, the velocity of propagation is continually diminished, till at length, when the mixture has been brought to the very limit of inflammability, the progress of the combustion may be traced with the naked eye.

The temperature and composition of the flame of a mixture of carbon monoxide and oxygen have also been investigated by Deville (*Bull. Soc. Chim.* [2] v. 111). When a mixture of these gases in the combining proportions (2 vol. CO to 1 vol. O) issues under slight pressure from a jet having an area of 5 square millimetres, a flame 70 to 100 mm. high is formed, consisting of an inner and an outer cone. The outer cone, in which the combustion takes place, is deep blue at the base, yellowish or nearly colourless towards the apex; in the inner cone, which is only 10 mm. high, no combustion goes on, because the rapidity of displacement of the molecules is there superior to the very slow rate of propagation of heat in the mixture (*vid. sup.*). To collect the gases from the different parts of the flame, a silver tube pierced with a small aperture was placed across it in the part to be examined, and the gases were aspirated by passing a rapid stream of water through the tube. They are thus rapidly cooled, pass along the tube together with the water, and are finally collected by means of a bent delivery-tube in jars standing over a water-trough.

The temperatures and composition of the different parts of the flame are exhibited in the following table:

Height above the orifice	Corresponding Temperature	Composition of the gas		
		CO	O	N
67 mm.	Melting heat of silver, and above	0·2	21·3	78·5
54	Melting heat of gold	6·2	28·1	65·7
44	Commencing white heat of platinum	10·0	20·0	70·0
35	White heat of platinum	17·3	24·8	57·9
28	Strong white heat of platinum	19·4	26·5	54·1
18	Intense white heat of platinum	29·0	25·1	45·9
15	Incipient fusion of platinum	40·0	32·9	27·1
12	Melting heat of platinum	47·0	36·0	17·0
10 *	Sparkling of the melted platinum	55·3	35·3	9·4
10 †	Still higher temperature	55·1	36·5	8·4
0 ‡		64·4	33·3	2·3

* A little above the apex of the inner cone. † Somewhat below the apex of the inner cone.
‡ Original mixture.

These numbers show that the highest temperature is at the apex of the inner cone or a little below it; that the temperature gradually diminishes towards the apex of the flame; and that the quantity of carbon dioxide increases in the same proportion from the apex of the inner cone, whereas at most two-thirds of the carbon monoxide and oxygen enter into combination, to the vertex of the flame itself, where carbon monoxide can no longer be detected. At the apex and edges of the inner cone, the carbon monoxide and oxygen unite almost instantaneously, but only partially, on account of the very high temperature there existing.

2. *Luminosity of Flame.*—It has generally been supposed that the light-giving power of a flame depends essentially on the presence of solid incandescent particles; and there is no doubt that the luminosity of a gaseous flame is very greatly increased by introducing into it a solid substance which can be raised by it to a very high temperature. Frankland has, however, shown that it is possible to produce very bright flames without the intervention of solid matter. Metallic arsenic burnt in a stream of oxygen produces an intense white flame, although both the metal itself and the product of its combustion (arsenious oxide) are gaseous at the temperature of the flame. The combustion of a mixture of nitrogen dioxide and carbon bisulphide also produces a dazzling white flame, without any separation of solid matter.

The conditions most essential to luminosity in a flame are a high temperature and the presence of gases or vapours of considerable density. The effect of high temperature is seen in the greater brightness of the flame of sulphur, phosphorus, and indeed all substances, when burnt in pure oxygen, as compared with that which results from their combustion in common air. The relation between the luminosity of a flame and the vapour-densities of its constituents may be seen from the following table, in which the vapour-densities are referred to that of hydrogen as unity:

Relative densities of gases and vapours.

Hydrogen	1	Arsenious chloride . .	9¾
Water	9	Phosphoric oxide .	71, or 142
Hydrochloric acid . .	18¼	Metallic arsenic . .	150
Carbon dioxide . . .	22	Arsenious oxide . .	198
Sulphur dioxide . . .	32		

A comparison of these numbers shows that the brightest flames are those which contain the densest vapours. Hydrogen burning in chlorine produces a vapour more than twice as heavy as that resulting from its combustion in oxygen, and accordingly the light produced in the former case is stronger than in the latter; carbon and sulphur burning in oxygen produce vapours of still greater density, namely, carbon dioxide and sulphur dioxide, and their combustion gives a still brighter light; lastly, phosphorus, which has a very dense vapour, and likewise yields a product of great vapour-density, burns in oxygen with a brilliancy which the eye can scarcely endure. Moreover, the luminosity of a flame is increased by condensing the surrounding gaseous atmosphere, and diminished by rarefying it. The flame of arsenic burning in oxygen may be rendered quite feeble by rarefying the oxygen; and on the contrary the faint flame of any ordinary spirit lamp becomes very bright when placed under the receiver of a condensing pump. Frankland has also found that candles give much less light when burning on the top of Mont Blanc than in the valley below, although the rate of combustion in the two cases is nearly the same (i. 1100). The effect of condensation in increasing the brightness of a flame is also strikingly seen in the combustion of a mixture of oxygen and hydrogen, which gives but a feeble light when burnt under the ordinary atmospheric pressure, as in the oxy-hydrogen blowpipe, but a very bright flash when exploded in the Cavendish eudiometer, in which the water vapour produced by the combustion is prevented from expanding.

Under a pressure of ten atmospheres, the flame of hydrogen, and still more that of carbon-monoxide burning in oxygen, gives a bright light and a continuous spectrum. The electric spark is more luminous in proportion as the gas or vapour through which it passes has a greater density. The feeble light produced by the combustion of phosphorus in chlorine, which yields a very dense product, (PCl^5), appears to be due to the low temperature of the flame. Strongly heated phosphorus-vapour burns in hot chlorine with a dazzling white light.

The brightness of ordinary lamp, candle, and gas flames is due, not, as commonly supposed, to the separation of solid particles of carbon, but to that of very dense hydrocarbons, which produce the same effect as the vapours of arsenic and phosphorus in their respective flames. That such is the case is shown, first by the perfect transparency of the flame, which is quite inconsistent with the presence of solid particles;

secondly by the nature of the soot or lampblack deposited from it, which is well known not to consist of pure carbon, but to contain considerable quantities of hydrogen (Frankland, *Journal of Gas-lighting*, July 1867, p. 291; *Proc. Roy. Soc.* xvi. 419).

3. *Conditions of Explosion* (Abel, *Phil. Trans.* 1869; *Chem. Soc. J.* [2] viii. 41; abstr. *Proc. Roy. Soc.* xvi. 395).—The degree of rapidity with which an explosive substance undergoes metamorphosis, as also the nature and results of such change, are in the greater number of instances susceptible of several modifications, by variation of the circumstances under which the conditions essential to chemical change are fulfilled. Excellent illustrations of the modes by which such modifications may be brought about are furnished by gun-cotton, which may be made to burn very slowly and almost without flame, to inflame with great rapidity but without development of great explosive force, or to exercise a violent destructive action, according as the mode of applying heat, the circumstances attending its application, and the mechanical conditions of the explosive agent are modified. In general, the explosion is more violent and the combustion more complete in proportion to the amount of resistance offered at the commencement of the combustion to the escape of the gases—in other words, in proportion as the strength of the receptacle enclosing the gun-cotton, and the consequent initial pressure developed by the explosion, is increased. (See PYROXYLIN, iv. 779.)

Other explosive compounds and mixtures are similarly influenced by the circumstances attending their metamorphosis. A charge of *gunpowder* in a cylindrical tin case, fired by a fuse inserted near the bottom, explodes much more violently than the same charge ignited by a fuse placed just beneath the surface; in the first instance the main body of the charge acts at the moment of ignition as tamping does in a blast-hole, by presenting a resistance to the escape of the gases generated, and thus for a moment establishing the pressure essential to the violent and perfect explosion of the powder first inflamed, whereupon the same character of explosion extends throughout the charge. In like manner *mercuric fulminate* (50 grains) inflamed by bringing an incandescent platinum wire just in contact with the surface or edge of the heap, explodes with a dull report, and produces no effect on a flat plate of copper sheet on which it rests; but a much smaller quantity (15½ grains) of the same fulminate heaped up over the platinum wire produces a sharp and violent explosion, the force of which deeply indents and bends up the support of sheet copper.

The volume of the explosion of a small quantity of *silver fulminate* confined in a case of stout sheet metal is very decidedly greater than if a corresponding quantity be enclosed in metal foil, or freely exposed to air and inflamed in the same manner. The violence of explosion of *iodide of nitrogen* is very decidedly increased by enclosing it in an envelope or shell of plaster of Paris, or, better still, in a case of sheet metal, while the *chloride of nitrogen* explodes with but comparatively little violence, unless it is confined. The reputation which this substance has enjoyed of being the most violent explosive body known, appears to be due to the fact that experiments on its explosion have always been conducted with a covering of water upon the material. Three or fours drops (about 0·14 grm. = 2 grains) placed in a watch-glass covered only with a thin layer of water, explode with a sharp report when touched with turpentine, and almost pulverise the glass; but similar quantities, of which the upper surfaces were exposed to air, have been repeatedly exploded in watch-glasses without breaking them. Two grms. of the chloride, contained in a watch-glass, and covered with a thin layer of water, were placed upon a small solid cylinder of hard *papier mâché* which rested upon paving. A violent explosion was produced by touching the chloride with turpentine, the watch-glass was pulverised and dispersed, and the cylinder was greatly shattered, fragments being projected in all directions. Four grms. of the chloride, with the upper surface exposed to air and placed upon a similar cylinder of *papier mâché*, produced a comparatively very feeble explosion; the watch-glass was broken, but the cylinder was not in the slightest degree affected, and remained undisturbed in its original position. A repetition of the experiment with 4 grms. of the chloride, enclosed by a thin layer of water, produced complete disintegration of the cylinder. It appears from these results that, in the case of the chloride of nitrogen, the decomposition of which is of an instantaneous character, the resistance offered at the moment by the layer of water acts as effectually in intensifying the force of explosion as a thin sheet-metal case does with the mercuric fulminate, or as a strong iron shell with gun-cotton or gunpowder.

Nitroglycerin or *Glonoïn*, which bears some resemblance to chloride of nitrogen in the suddenness of its explosion, requires the fulfilment of special conditions for the full development of its explosive force. Its explosion by the simple action of heat can be accomplished only when the source of heat is applied for a considerable time in such a way that chemical decomposition is established in some portion of the mass, and is favoured by the continued application of heat to that part. Under these circumstances the chemical change proceeds with very rapidly accelerating violence, and eventually brings about a sudden transformation of the heated portion into gaseous products, which transformation is instantly communicated throughout the mass of nitroglycerin, so that confinement of the substance is not necessary to develop its full explosive force. This result can be obtained more expeditiously, and with greater certainty, by exposing the substance to the concussive action of a detonation produced by the ignition of a small quantity of fulminating powder, closely confined and placed in contact with or near to the nitroglycerin.

The development of the violent explosive action of nitroglycerin freely exposed to air through the agency of a detonation was regarded until recently as a peculiarity of that substance; but Abel's experiments have shown that gun-cotton and other explosive compounds and mixtures do not necessarily require confinement for the full development of their explosive force, this result being obtained (and very readily in some instances, especially in that of gun-cotton) by means similar to those applied in the case of nitroglycerin, viz. by the percussive action of a detonation.

The action of a detonation in determining the violent explosion of gun-cotton, nitroglycerin, &c., cannot be ascribed to the direct operation of the heat developed by the chemical changes of the charge of detonating compound used as the exploding agent. An experimental comparison of the mechanical force exerted by different explosive compounds, and by the same compound employed in different ways, has shown that the remarkable power exhibited by the explosion of small quantities of certain bodies (the mercuric and argentic fulminates) to accomplish the detonation of gun-cotton, while comparatively large quantities of other highly explosive agents are incapable of producing this result, is generally accounted for in a satisfactory manner by the difference in the amount of force suddenly brought to bear in the different instances upon some portion of the mass operated upon. Most generally, therefore, the degree of facility with which the detonation of a substance will develop similar change in a neighbouring explosive substance may be regarded as proportionate to the amount of force developed within the shortest space of time by that detonation, the latter being, in fact, analogous in its operation to that of a blow from a hammer or of the impact of a projectile.

Several remarkable results of an exceptional character have, however, been obtained, which indicate that the development of explosive force under the circumstances referred to is not always simply ascribable to the sudden operation of mechanical force. Thus silver fulminate, which explodes much more suddenly and with much more powerful local force than mercuric fulminate, nevertheless, when applied under the same conditions, does not induce the explosion of gun-cotton so readily as mercuric fulminate. 5 grains of mercuric fulminate enclosed in a case of stout sheet metal and exploded in close contact with compressed gun-cotton, caused the detonation of the latter; but 5 grains of silver fulminate enclosed in tin-foil, though it appeared to produce quite as sharp a detonation as the same quantity of the mercury salt enclosed in the stout case, did not explode gun-cotton with which it was surrounded, but merely scattered the mass; when enclosed in the stout sheet-metal case, however, the 5 grains of silver fulminate accomplished the detonation of the gun-cotton. Iodide and chloride of nitrogen are much more susceptible of sudden explosion even than silver fulminate; nevertheless the iodide does not appear to be capable of causing the explosion of compressed gun-cotton; and the chloride of nitrogen shows but little capability of producing the same effect, 50 grains being the smallest quantity that will answer the purpose. Lastly, it is found that nitroglycerin when exploded by a charge of mercuric fulminate will not bring about the explosion of compressed gun-cotton placed in contact with it, though under precisely similar circumstances the explosion of gun-cotton or of nitroglycerin will induce the explosion of a larger mass of its own kind.

These results point to the conclusion that the effect of the detonation of one substance in causing the explosion of another depends not only on the force, but also on the *nature* of the vibrations developed in the former, the most probable explanation of the observed results being that the vibrations attendant upon a particular explosion, if synchronous with those which would result from the explosion of a neighbouring substance in a state of high chemical tension, will, by their tendency to develop those vibrations, either determine the explosion of that substance, or, at least, greatly aid the disturbing effect of mechanical force suddenly applied, while, in the instance of another explosion, which develops vibratory impulses of a different character, the mechanical force applied through its agency has to operate with little or no aid, so that greater force or a more powerful detonation is required in the latter case to accomplish the same result.

Instances of the apparently simultaneous explosion of numerous distinct and even somewhat widely separated masses of explosive substances (such as simultaneous explosions in several distinct buildings at powder-mills) occur not unfrequently, in which the generation of a disruptive impulse by the first or initiative explosion, which is communicated with extreme rapidity to contiguous masses of the same nature, appears much more likely to be the operating cause, than that the simultaneous explosion should be brought about by the direct operation of heat and mechanical force developed by the starting explosion.

The explosion of gun-cotton and gunpowder by the agency of detonation is much more sudden and violent than when the same substances are exploded, even in confined spaces, by the simple agency of heat. This has been abundantly proved, in the case of gun-cotton, by blasting operations in various descriptions of rock, and by measurement of the comparative destructive effect of charges exploded under water. Charges of gun-cotton contained in blast-holes, and having a detonating fuse inserted in or placed immediately over them, have produced much greater rending and shattering effects in hard rock and in wood (although the blast-holes were left entirely open, or only filled with loose sand, earth, or powdered rock) than corresponding charges applied in similar positions, but fired with ordinary fuses, although in the latter instances the gun-cotton was confined by 'tamping,' or firmly closing the blast-hole to a considerable depth. A series of systematic experiments has been carried on at Chatham by the Government Committee on Floating Obstructions, with the view of comparing the destructive power of gunpowder and gun-cotton, in which charges of these materials were exploded in proximity to submerged targets, with systematic variations of the strength of the cases containing the charges, the depth of their immersion beneath the surface, and their distances from the targets. The results of these experiments warranted the conclusion that gun-cotton, when confined in cases of sufficient strength to develop its full explosive action, exerts a destructive effect equal to about five times that of gunpowder. A few experiments to compare with these have been recently instituted with charges of gun-cotton enclosed in thin sheet-metal cases and exploded by means of detonating fuses, and in these the destructive action upon vertical targets, placed at very considerable distances from the charges, was from ten to twelve times greater than that of gunpowder. The concussion imparted through the water to considerable distances, by the explosion of small charges (2 to 3 lb.) of gun-cotton in the new manner, very greatly exceeded in their effects the results produced by the explosion of submerged charges by the ordinary method.

An examination of the decomposition-products of gun-cotton exploded by detonation has shown that they do not differ in any important respect from those obtained by the complete metamorphosis of the substance when exploded in strong shells under ordinary conditions (iv. 779). The increased destructive effect developed by the explosion through the agency of detonation must therefore be ascribed to the greater rapidity of the explosion under these conditions. The ordinary explosion of gun-cotton is attended by a considerable body of flame, due to the ignition of the generated carbonic oxide; but the detonation of gun-cotton is attended only by a sudden flash, which it is very difficult to observe in daylight if only small quantities are exploded. The transformation of the solid into gas appears, in fact, to be too sudden for the generated combustible gas to become inflamed.

CONCHININE. Syn. with QUINIDINE.

CONESSINE. Syn. with WRIGHTINE (v. 1048).

CONHYDRINE. $C^8H^{17}NO = \left.\begin{matrix}(C^8H^{15}O)''\\H\end{matrix}\right\}N$ (ii. 1).—Wertheim (*Wien. Akad. Ber.* xlvi. [2] 299) obtained from 333 kilogrms. of fresh hemlock-seeds 700 grms. of pure conine, and rather more than 40 grms. of pure conhydrine, the greater part of the latter being obtained by fractional distillation of the crude conine, a smaller portion from the residues in the still. These residues, after neutralisation with sulphuric acid and filtration from the separated gypsum, were evaporated to dryness, exhausted with strong alcohol, and the extract again evaporated was agitated with strong potash-ley and ether; the conhydrine which remained after spontaneous evaporation was obtained pure by one recrystallisation from ether.

Conhydrine melts at 120·0°, and boils at 225·45° (bar. at 719·8 mm.). It is not acted upon by nitrous acid, but by phosphoric anhydride or by sodium it is converted ne. With mercuric oxide it resinises without giving off gas. *Conhydrine* which is easily soluble in water and in alcohol, crystallises in flat, rather hard prisms; the *nitrate* is somewhat less soluble, and gradually solidifies to a crystalline mass. The *hydrochloride* and *acetate* are uncrystallisable.

Ethyl-conhydrines.—When conhydrine is heated with ethyl iodide, a brisk reaction takes place, and ethyl-conhydrine hydriodide, $C^8H^{16}(C^2H^5)NO.HI$, is obtained, as an easily soluble crystalline mass; and this, when decomposed by potash-ley, yields ethyl-conhydrine as an oil which also solidifies in the crystalline form. It distils without decomposition, and is more soluble in ether than conhydrine. Heated with ethyl iodide, it solidifies to a mass consisting of diethyl-conhydrine hydriodide, $C^8H^{15}(C^2H^5)^2NO.HI$, which gradually separates from its almost syrupy aqueous solution, in small hard crystals, having an almost adamantine lustre, and consisting, according to measurements by Zepharovich (*Wien. Akad. Ber.* xlvii. [1] 275), of rhombic sphenoïdo-hemihedral combinations of $+\frac{P}{2}, -\frac{P}{2}, oP, \breve{P}\infty$, the face $\frac{P}{2}$ generally occurring alone. Axes $a : b : c = 0·8823 : 1 : 105$. This salt decomposed with silver oxide yields a caustic bitter syrup which rapidly absorbs carbonic acid. The *hydrochloride* of this ammonium-base is very soluble in water and crystallises slowly in thin needles; the *platinochloride*, $[C^8H^{14}(C^2H^5)^2NO.Cl]^2.PtCl^4$, is a light wine-yellow precipitate which separates from hot water in beautiful orange-red crystals consisting, according to Zepharovich, of quadratic combinations $P.2P.9P.\infty P$. For P, the ratio of the secondary axes to the principal axis is 1 : 0·8679. Angle P : P (terminal) = 113° 31′; P : P (basal) = 78° 21′; 2P : 2P (terminal) = 98° 11′; 2P : 2P (basal) = 135° 40′; 9P : 9P (terminal) = 90° 28′; 9P : 9P (basal) = 169° 39′.

Azoconhydrine. $C^8H^{16}N^2O$.—The near agreement of the vapour-density, 5·39, calculated from this formula with that found by experiment (in three experiments, 5·437, 5·691, and 5·410) shows that the formula $C^{32}H^{64}N^8O^4$ originally given to this substance (ii. 964) was too high. *Nascent hydrogen* (zinc and hydrochloric acid) converts azoconhydrine into conine:

$$C^8H^{16}N^2O + H^4 = C^8H^{15}N + H^2O + NH^3.$$

When azoconhydrine is heated to 160° with metallic *sodium* broken into small pieces by agitation while in the melted state, it gives off a large quantity of gas (11·5 p. c. hydrogen to 88 nitrogen), and leaves a residue containing a large quantity of conine, together with unaltered azoconhydrine; perhaps thus:

$$\underset{\text{Azoconhydrine.}}{4C^8H^{16}N^2O} + 10Na = \underset{\text{Conine.}}{4C^8H^{15}N} + \underset{\text{Sodamide.}}{2NH^2Na} + \underset{\text{Sodium oxide.}}{4Na^2O} + N^2$$

and

$$2C^8H^{16}N^2O^2 + 4Na = 2C^8H^{15}N + 2Na^2O + N^2 + H^2.$$

Azoconhydrine dissolves abundantly in concentrated acetic or formic acid, and absorbs large quantities of anhydrous hydrocyanic acid, but the resulting compounds are decomposed by water and by heating to 100° (Wertheim, *Wien. Akad. Ber.* xlvii. [2] 491).

CONIFERIN. $C^{24}H^{32}O^{12}$ (Kubel, *J. pr. Chem.* xcvii. 243; *Jahresb.* 1866, p. 675).—A glucoside occurring in the cambium of coniferous woods (*Abies excelsa*, *A. pectinata*, *Pinus Strobus*, *P. Cembra*, *Larix europæa*). It forms needle-shaped crystals containing $C^{24}H^{32}O^{12}.3H^2O$, which effloresce in dry air and give off all their water at 100°; melts at 185°, and carbonises at a higher temperature, giving off the odour of caramel; dissolves easily in hot water, sparingly in cold water and in alcohol, and is insoluble in ether. The aqueous solution tastes faintly bitter, and turns the plane of polarisation to the left. Boiled with dilute acids it gives off an odour of vanilla, and deposits a resinous body insoluble in alkalis, while the filtrate contains a dextrogyrate sugar. Strong sulphuric acid in contact with coniferin or the resinous body just mentioned acquires a characteristic dark violet colour, and on adding water a precipitate is formed which gives to the liquid an indigo-blue colour. By this reaction coniferin may be detected in coniferous woods, namely, by moistening a fresh section with strong sulphuric acid; the young wood and the bast exhibit a violet colour.

CONINE. $C^8H^{15}N$.—Schiff (*Ann. Ch. Pharm.* clvii. 352) has obtained this base synthetically by heating normal butyric aldehyde, C^4H^8O, with alcoholic ammonia, whereby a base, *dibutyraldine*, $C^8H^{17}NO = 2C^4H^8O + NH^3 - H^2O$, is obtained, and subjecting this base to dry distillation: $C^8H^{17}NO - H^2O = C^8H^{15}N$.

CONYLENE. C^8H^{14} (ii. 964).—This hydrocarbon, produced by the action of phosphoric anhydride on azoconhydrine, is mixed with a less volatile body not yet examined. It does not appear to be poisonous.

When 9 pts. (1 mol.) conylene-bromide, $C^8H^{14}Br^2$, are heated to 120°–140°, with

11 pts. (2 mol.) silver acetate and a small quantity of glacial acetic acid, conylene diacetate, $(C^8H^{14})''(C^2H^3O^2)^2$, is formed, having an acid reaction, an odour of peppermint, a sp. gr. of 0·988 at 18·2°, and boiling at 225°. This acetate, distilled with pulverised potassium hydrate at a temperature above 230°, gives off, first a pale yellow oily liquid, and then a smaller quantity of a very viscid distillate. The latter is lighter than water, insoluble therein, but soluble in alcohol and ether, and has the composition of conylene alcohol, $(C^8H^{14})''(HO)^2$. The more volatile distillate has the composition of diconylene alcohol, $C^{16}H^{30}O^3$ or $(C^8H^{14})^2H^2O^3$, but the lower boiling point renders this view of its constitution somewhat improbable (Wertheim, *loc. cit.*).

COOKEITE. A silicate occurring, together with red tourmaline and lepidolite, in the granite formation of Hebron and Paris in the State of Maine. It is white, sometimes yellowish-green, with a nacreous lustre; hardness = 2·5; sp. gr. = 2·70. Its analysis gave 34·93 p. c. SiO^2, 44·91 Al^2O^3, 2·57 K^2O, 2·82 Li^2O, 0·47 SiF^4, 13·41 H^2O, and 0·38 hygroscopic water, a composition nearly the same as that of euphyllite and margarite (G. J. Brush, *Sill. Am. J.* [2] xli. 246).

COPAIBA BALSAM. According to Roussin (*J. Pharm.* [4] i. 221), the hardening of this balsam by lime or magnesia depends upon the presence of a certain quantity of water (about $\frac{1}{50}$ of the balsam), the lime or magnesia being thereby converted into a hydrate which unites with the balsam.

The variety of copaiba balsam from Maracaibo in Columbia has been examined by Strauss (*Ann. Ch. Pharm.* cxlviii. 148; *Zeitschr. f. Chem.* [2] v. 301). It has a wine-yellow colour, syrupy consistence, and sp. gr. = 0·900 at 15°; dissolves in all proportions in alcohol, ether, and benzol. With ammonia it forms a clear solution, which becomes turbid on addition of a large quantity of water, and with magnesia a plastic soapy mass; it is coloured brown-red by strong sulphuric acid; does not smell like turpentine when heated.

On boiling this balsam with weak soda-ley, the greater part of the volatile oil separates on the surface. This oil, when dehydrated over calcium chloride and rectified, is limpid, has a pleasant aromatic odour and burning bitter taste. Sp. gr. 0·921 at 10°. Boiling point 250°–260°. It dissolves in ether, benzol, and chloroform, in about 3 pts. of cold absolute alcohol, more readily in hot alcohol, and separates from this solution on cooling. It is coloured yellow by dilute nitric acid, deep red by nitric acid of sp. gr. 1·41, the latter after a few minutes oxidising it violently, and forming a resinous mass which dissolves at the heat of the water-bath in the supernatant liquid, the solution when evaporated leaving a resinous residue soluble with red colour in potash-ley; hydrochloric acid added to the potash solution throws down an amorphous substance soluble in alcohol. The vapour-density of the oil, which is nearly 9·5, shows that its molecular formula is $C^{20}H^{32}$.

Metacopaivic Acid. $C^{22}H^{34}O^4$.—When the alkaline resin-solution decanted from the volatile oil is mixed with sal-ammoniac, the resin-soaps rise to the surface together with the volatile oil still dissolved in the liquid; and on adding hydrochloric acid to the ammoniacal solution filtered through moistened paper, metacopaivic acid rises to the surface in the form of a flocculent substance which may be dried in the air, and purified by repeated crystallisation from boiling alcohol. It crystallises in laminæ, dissolves in alcohol and ether, in petroleum only when heated; is insoluble in water; melts at 205°–206°; has an acid reaction; and decomposes carbonates. Its neutral solution in ammonia forms white precipitates with calcium, barium, and lead salts. The *silver salt* $C^{22}H^{32}O^4Ag^2 + H^2O$ is sparingly soluble in water, easily soluble in ammonia, and becomes anhydrous at 150°. The *cupric salt* $C^{22}H^{32}O^4Cu \cdot H^2O$ is a bluish-green precipitate. The *sodium salt* forms very hygroscopic crystals.

The quantity of metacopaivic acid in the balsam is very small. Strauss regards it as probably identical with Werner's gurgunic acid obtained by treating wood-oil or gurgun balsam (i. 495) with potash-ley, although the melting point of the latter, as given by Werner (*Jahresb.* 1862, p. 462), is 14° or 15° higher.

According to Flückiger (*J. pr. Chem.* ci. 235), Maracaibo balsam is optically dextrogyrate, Maranha balsam lævogyrate, and a mixture of the two in certain proportions is optically inactive.

COPPER. *Atomic Weight* 63·4. Equivalent 31·7.—Field a. Abel (*Chem. Soc. J.* [2] i. 89) have examined the impurities in native copper from several localities. In thick plates of copper from Chile (the so-called *Charqui copper*) covered on both sides with talc and chlorite, they found only traces of bismuth and silver. Two specimens of Minnesota copper from Lake Superior contained 0·56 p. c. silver without any other admixture; a third consisted, to about $\frac{1}{4}$ of its entire mass, of native silver, occurring in thick veins and containing a trace of lead. A specimen of Siberian copper, occurring with green altered arragonite and superficially converted into red copper ore, was found to be very impure, containing 1·28 p. c. arsenic, together with small quantities of silver, bismuth, and lead. Native copper from Algadon Bay in Bolivia was found by v. Bibra (*J. pr. Chem.* xcvi. 193) to contain, on the average, 97·5 p. c. copper, 2·0 iron, 0·3 silicon, and a trace of antimony.

Copper is contained to the amount of 5·9 p. c. in *turacin*, the red pigment of the wing-feathers of the Turaco (Church, *Chem. News*, xix. 265).

Metallurgy.—A method of extracting copper from poor ores containing lime or dolomite is described by G. Bischof (*Lond. Journal of Arts*, 1862, p. 277; *Dingl. pol. J.* clxv. 31; *Jahresb.* 1862, p. 649). It consists essentially in igniting the ores (in a lime-kiln) at a moderate heat, partly removing the lime and magnesia by washing, and fusing the residue with iron pyrites (5 pts. to 1 pt. of copper) to obtain *coarse metal* (ii. 23). The latter is finely pulverised, and roasted in muffle-furnaces for a long time at a low red heat, and the roasted product is lixiviated, whereby it is resolved into a solution of cupric sulphate and a residue from which the cupric oxide is extracted by dilute sulphuric acid. The copper is then precipitated from the sulphate solution by metallic iron, washed with liquids containing copper, freed from arsenic and antimony by roasting, and finally melted. A method of extracting copper from poor sulphurous ores, practised at Foldal in Norway, is described by C. Weltz (*Dingl. pol. J.* clxiv. 289; *Jahresb.* 1862, p. 648). See also H. Wagner (*Dingl.* clxxxiii. 338; *Jahresb.* 1867, p. 889); Aubel (*Dingl.* clxxxiv. 137; *Jahresb. ibid.*). Chiado (*Dingl.* clxxx. 360) describes a process for obtaining refined copper at one operation from sulphuretted ores. It consists essentially in smelting the roasted ore with charcoal in a furnace so constructed that the coarse copper, as it is formed, may run off into a reverberatory furnace, where it is converted into refined copper by the united action of air and over-heated steam.

An examination of the products of the Mannsfeld process (i. 31) in its several stages has been made by G. Steinbeck (*Inaugural Dissertation*, Halle, 1862; *Jahresb.* 1862, p. 643).

Many kinds of pyrites which are burnt for the preparation of sulphuric acid contain sufficient copper to render its extraction from the residues remunerative. Haeffelly (*Lond. Journal of Arts*, May 1862, p. 278; *Rép. Chim. app.* iv. 384) roasts these residues a second time, lixiviates the product with an acid solution of manganous chloride (residues of chlorine manufacture), and precipitates the copper from the resulting solution (which must contain free acids) by means of the basic calcium sulphide of the soda manufacture. The precipitated sulphide is then treated by the ordinary methods. For other methods of treating these cupriferous pyrites residues, see Richardson and Watts's *Chemical Technology*, pt. iii. p. 73, and pt. v. p. 206.

For the electrolytic precipitation of copper from poor cementation-waters (ii. 36), Patera (*Dingl.* clxxxiv. 134) passes the solutions slowly through an apparatus in which the positive pole is formed of iron plates immersed in a porous cell containing hydrochloric acid or solution of common salt, and the negative pole of granulated copper or coke connected with the iron by a copper wire.

Impurities in Commercial Copper. — The quantities of different non-metallic impurities, especially oxygen, in several kinds of refined copper have been determined by Abel (*Chem. Soc. J.* [2] ii. 164). Ingots of Kapunda copper (which is remarkably free from metallic impurities) having depressions on their upper surface were found to contain a larger proportion of cuprous oxide (1·704 to 2·631 p. c.) than those with even surface (0·856 to 1·409 p. c.); the latter also exhibited a regular decrease in the proportion of cuprous oxide from the surface to the middle of the bar. Copper fused in a crucible lined with charcoal and left to solidify without access of air, did not contain a trace of cuprous oxide if the fusion had been long continued; in the contrary case it was found to contain a small quantity (0·13 to 0·19 p. c.). When the copper fused in the charcoaled crucible was cooled in contact with the air, spitting took place shortly before complete solidification, and the metal then contained oxygen. Several varieties of copper from the Haford works gave the following percentages of cuprous oxide:

	Cuprous oxide in 100 parts
Overpoled copper	0·228 to 0·357
Tough-pitch copper	0·223 „ 0·321
Half-poled copper	1·616 „ 1·873
Dry copper, inner portion	3·750 „ 3·782
„ „ outer portion	4·531 „ 4·603

Carbon was not detected with certainty in Alten and Kapunda copper remelted with charcoal; but Alten copper and a specimen from North America were found to contain a trace (at most 0·003 p. c.) of *selenium*; copper from Copiapo, Manilla, and Hungary was found to be free from that element. The amount of *sulphur* found in various kinds of copper, by four hours' ignition in a stream of hydrogen, was about 0·005 p. c.; phosphorus and nitrogen could not be detected.

Detection and Estimation.—A borax bead containing only a small quantity of copper remains transparent and colourless when heated in the reducing flame, and then left to cool, especially if the bead itself is not very large and the heating has been long continued. If gently heated again it becomes ruby-coloured and transparent, but the colour disappears if the heat is too strong (Gerland, *Bull. Soc. Chim.* [2] i. 271).

For quantitative estimation copper may be precipitated:

α. In the metallic state, by electrolysis. The solution of the sulphate is poured into a small platinum dish serving as the negative pole of a battery of one or two elements, the positive pole being formed by a thick platinum wire dipping into the solution. The copper, which is deposited in the dish in a few hours in the form of a shining film, is washed with distilled water, dried over sulphuric acid in a vacuum, and weighed in the dish (W. Gibbs, *Sill. Am. J.* [2] xxxix. 58). See also Luckow (*Jahresb.* 1865, p. 685). Ullgren (*Zeitschr. f. Chem.* [2] v. 307) uses for this purpose a glass tube half an inch wide, closed at the bottom with a piece of bladder, and loosely at the top with a cork, through which a strip of zinc may be moved up and down. The tube filled to $\frac{5}{6}$ with solution of common salt is immersed to a small depth into the copper solution acidulated with sulphuric acid; and the strip of zinc dipping into the salt-solution is connected with a piece of platinum foil, on which is placed the platinum dish containing the copper solution. The rate of deposition of the copper may be regulated by immersing the zinc more or less deeply in the salt-solution; the more slowly it takes place the more compact is the deposit.

β. Copper may be estimated as cuprous sulphide, Cu^2S (containing 79·85 p. c. copper), by precipitating it as cupric sulphide from the solution of the sulphate or chloride with hydrogen sulphide, and strongly igniting the washed and dried precipitate in a porcelain crucible through which a stream of hydrogen is directed by a tube passing through the perforated platinum lid (H. Rose, *Pogg. Ann.* cx. 120). In precipitating copper with hydrogen sulphide, it is best to keep the solution at the boiling heat; the precipitate is then compact and does not oxidise in washing. The copper may also be at once precipitated as cuprous sulphide by addition of sodium hyposulphite to the solution of the sulphate, previously freed from hydrochloric and nitric acids by evaporation to dryness with sulphuric acid (Flajolot, *Ann. Ch. Phys.* [3] xxxix. 460). The precipitate is ignited, as above, in an atmosphere of hydrogen, to expel any excess of sulphur that it may contain.

γ. Gibbs (*Zeitschr. anal. Chem.* vii. 255, 422) precipitates the copper as cuprous hydride, Cu^2H^2, by adding magnesium hypophosphite in excess to a moderately dilute solution of cupric sulphate containing a slight excess of sulphuric acid, but free from nitric or hydrochloric acid (in presence of nitric acid the precipitation is incomplete; hydrochloric acid interferes with it by forming cuprous chloride). The solution is gradually heated to 80° or 90° to ensure the complete precipitation of the cuprous hydride; and the latter, after washing and drying, is ignited in a stream of hydrogen, whereby it is resolved into hydrogen gas and metallic copper, which is weighed. The process may be applied to the valuation of copper ores, the ore being first roasted in the finely divided state, then heated to low redness with a mixture of equivalent quantities of nitrate and acid sulphate of potassium, and the fused mass heated with a quantity of strong sulphuric acid, sufficient to convert the whole of the potassium into acid sulphate. The filtered aqueous solution is then to be treated as above.

δ. As Cuprous Iodide, Cu^2I^2. The copper solution, not containing excess of nitric acid, is mixed with excess of sulphurous acid, and then gradually with a solution of iodine in sulphurous acid. The precipitate, after standing for twelve hours, and washing, is converted into cupric oxide by suspending it in water, treating it with chlorine, and precipitating with potash (Flajolot, *loc. cit.*). Pisani (*Compt. rend.* xlvii. 294) collects the precipitated cuprous iodide on a weighed filter, dries it at 100°-120°, and weighs it; but this method appears to be troublesome. Pisani also recommends potassium iodide as a precipitant; but, according to Flajolot, the cuprous iodide is slightly soluble in excess of this reagent.

ε. As Cuprous Sulphocyanate, $Cu^2(CNS)^2$. The cupric solution free from nitric acid is reduced by sulphurous acid, and precipitated by potassium sulphocyanate, and the precipitated cuprous sulphocyanate is dried and weighed: it contains 52·5 p. c. copper. Or the precipitate may be converted into cuprous sulphide by fusion with sulphur in a covered crucible (Rivot, *Compt. rend.* xxxviii. 868). This method is recommended by Wolfskron (*Chem. Centr.* 1866, p. 255) for separating copper from palladium.

The precipitation of copper as cuprous iodide or sulphocyanate is better adapted than the ordinary mode of precipitation with hydrogen sulphide for effecting the complete separation of copper from zinc, nickel, cobalt, and manganese.

For estimating the quantity of cuprous oxide (or oxygen) present in refined copper, Abel (*Chem. Soc. J.* [2] ii. 164) recommends the following process, based upon the fact that neutral silver nitrate is decomposed by cuprous oxide, with separation of metallic silver, and formation of a basic cupric salt, which requires for conversion into neutral salt a quantity of acid equivalent to the cuprous oxide (or oxygen) present in the copper:

$$Cu^2O + 2NO^3Ag = Ag^2 + (NO^3)^2Cu.CuO.$$

A known weight of the copper under examination is digested for about three hours with a cold neutral solution of silver nitrate; and the portion unacted upon is picked out, thoroughly washed, and weighed, the difference between its weight and the original weight representing the quantity of copper acted upon by the silver nitrate. The mixture of precipitated silver and basic cupric nitrate is then collected, washed, and digested for half an hour with a known quantity of normal sulphuric acid (containing 1 pt. SO^4H^2 to 100 pts. water), after which the solution is filtered from the metallic silver, and the free acid in the filtrate is determined by alkalimetry. The quantity of acid neutralised by the cupric oxide is equivalent to the oxygen or the cuprous oxide in the metallic copper.*

The proportion of cuprous oxide in red copper ore may be estimated by digesting the finely pulverised mineral with dilute sulphuric acid and silver sulphate. Metallic silver is then separated in the proportion of 2 at. silver to 1 mol. cuprous oxide; $Cu^2O + SO^4H^2 = Cu + SO^4Cu + H^2O$, and $Cu + SO^4Ag^2 = SO^4Cu + Ag^2$ (Aubel, *Zeitschr. anal. Chem.* vi. 459). There must of course be no metallic copper present.

On the volumetric estimation of copper, see Galetta (*Zeitschr. anal. Chem.* 1869, 135; *Zeitschr. f. Chem.* [2] vi. 91).

Compounds of Copper with Non-metallic Elements.

Copper is a diatomic or bivalent metal, forming two series of compounds designated as *cupric* and *cuprous*. The compounds of both these series contain in their molecule 2 at. of a univalent, or 1 at. of a bivalent radicle, associated in the cupric compounds with 1 at. of copper, in the cuprous compounds with 2 at. of copper linked together by one of their units of affinity; in fact, the group —Cu—Cu—, composed of two diatomic atoms, is itself diatomic; *e. g.*,

Cupric compounds . . $Cu''Cl^2$; $Cu''O$; $Cu''(NO^3)^2$; $Cu''(SO^4)''$.
Cuprous compounds . . $(Cu^2)''Cl^2$; $(Cu^2)''O$; $(Cu^2)''(NO^3)^2$; $(Cu^2)''(SO^4)''$.

Cuprous Chloride, Cu^2Cl^2, may be obtained in the crystalline state by passing sulphurous acid gas into a solution of cupric sulphate mixed with an equivalent quantity of sodium chloride. The precipitated crystalline powder, consisting of small tetrahedrons, must be washed by decantation with aqueous sulphurous acid; if washed with pure water, it turns yellow, light brown, and violet, and in boiling water assumes a bright brick-red colour. It is so sensitive to light that the crystals, immersed in aqueous sulphurous acid and exposed to direct sunshine for only five minutes, acquire a complete copper colour and metallic lustre. This copper-coloured body is probably a cuprous oxychloride formed together with hydrochloric acid; when exposed to the air it oxidises, as quickly as the colourless crystals, to green cupric oxychloride (Wöhler, *Ann. Ch. Pharm.* cxxx. 373). Metallic copper dipped into solution of cupric chloride, ferric chloride, dilute nitromuriatic acid, or a solution of potassium chromate or chlorate mixed with hydrochloric acid, becomes covered with a whitish-grey film of cuprous chloride, which when exposed to light gradually becomes black, with copper reflex; this property may be made available for photography. In its original, as well as in its altered state, it is not perceptibly soluble in dilute nitric or sulphuric acid, but dissolves in sodium hyposulphite, potassium cyanide, iodine, potassium iodide, hydrochloric acid, and ammonium sulphate (Renault, *Compt. rend.* lix. 319; *Jahresb.* 1864, p. 278).

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* Abel has shown that the estimation of the oxygen by igniting the copper in hydrogen gas, as practised by Dick (*Phil. Mag.* [4] xi. 109), does not give exact results.

Cuprous Bromide, Cu^2Br^2, is formed in like manner by dipping a plate of copper into aqueous solution of cupric or ferric bromide, or into a solution of bromine in potassium bromide. It becomes distinctly blue in sunshine, much more slowly in diffused daylight, and then dissolves, though much less easily than the unaltered bromide, in hyposulphite or chloride of sodium (Renault).

Cuprous Iodide. Cu^2I^2.—A plate of copper exposed to the action of *iodine-vapour* or solution of iodine becomes covered with white crystalline cuprous iodide, which is much less sensitive to light than the chloride or the bromide. Both in its original and in its altered state this iodide is insoluble in sodium chloride and sulphite, potassium bromide and nitrate, and sal-ammoniac, but soluble in ammonia, sodium hyposulphite, and potassium cyanide, and in dilute hydrochloric, sulphuric, or nitric acid. An iodised copper plate exposed for a long time to light, and then immersed in a very weak solution of mercuric nitrate, becomes brick-red on the insulated parts, greenish on the unaltered parts (Renault).

A copper plate dipped into *cupric fluoride* and then exposed to light, becomes black and afterwards violet like the chlorinated plate (p. 493), though much more slowly; and the film is then much less soluble in hyposulphite or chloride of sodium than the original whitish-grey film (Renault).

Oxides.—Cuprous oxide of a fine red colour is easily obtained by heating 1 pt. cupric sulphate with ½ pt. sodio-potassic tartrate, 2 pts. cane-sugar, and 12 pts. water, then adding 1½ pt. sodium hydrate, and boiling for an hour (Böttger, *J. pr. Chem.* xc. 163).

Precipitated cuprous oxide dissolves in a concentrated aqueous solution of magnesium chloride, slowly at ordinary temperatures, more quickly at 100°, forming magnesium hydrate and cuprous chloride:

$$Cu^2O + MgCl^2 + H^2O = Cu^2Cl^2 + MgH^2O^2.$$

When cuprous oxide is dissolved to saturation in a warm solution of magnesium chloride, and the solution is left to cool without separating the magnesium hydrate, an orange-red precipitate of cuprous hydrate, or perhaps of cuprous oxychloride, is deposited, which dissolves when heated and reappears on cooling. When solid cuprous chloride is digested with magnesia and water, cuprous hydrate and magnesium chloride are produced. Nevertheless the double chloride of copper and magnesium is permanent in presence of magnesium hydrate, provided a considerable excess of magnesium chloride is also present. A filtered solution of cuprous oxide in magnesium chloride yields on dilution a precipitate of cuprous chloride coloured orange-yellow by adhering cuprous oxide. A mixed solution of magnesium sulphate and sodium chloride may also be used as a solvent of cuprous oxide (T. S. Hunt, *Compt. rend.* lxix. 1356; *Zeitschr. f. Chem.* [2] vi. 152).

Cuprous oxide and ferrous chloride yield ferric oxide, with partial reduction of the cuprous oxide to metal. This reduction may be effected by adding recently precipitated and still suspended ferrous hydrate to a solution of cuprous chloride in common salt, and gently warming the liquid. A similar result is obtained on adding a soluble ferrous salt to a non-filtered solution of cuprous oxide in magnesium chloride. Ferrous oxide also reduces cupric to cuprous chloride, and if present in sufficient quantity precipitates all the copper as metal. Cupric oxide, even after ignition, acts on a solution of ferrous chloride in the cold according to the equation: $3CuO + 2FeCl^2 = Cu^2Cl^2 + CuCl^2 + Fe^2O^3$. The reaction is greatly retarded by the insolubility of the cuprous chloride, but in presence of common salt, or when aided by heat, it goes on quickly and completely. When a solution of ferrous chloride and sodium chloride is digested with a large excess of cupric oxide, the latter unites with the cupric chloride produced, forming an insoluble oxychloride (Hunt, *loc. cit.*).

The mutual action of cupric and ferrous salts, resulting in the formation of cuprous oxide and a basic ferric salt, first studied by Levol (ii. 68), has also been investigated by Braun and Weith (*Zeitschr. f. Chem.* [2] iii. 568, 623; *Bull. Soc. Chim.* [2] viii. 409; ix. 214; *Jahresb.* 1867, p. 301).

Tetracupric oxide, $(Cu^4)''O$, Rose's *quadrantoxide of copper*, is prepared by treating a cooled solution of cupric sulphate with an alkaline solution of stannous chloride not in excess, whereby a blue precipitate of cupric hydrate is first formed, which after a while changes into yellow cuprous hydrate, and ultimately into olive-green tetracupric oxide: it must be washed, first with pure water, then with ammoniacal water in an atmosphere of hydrogen. This oxide, when exposed to the air, is quickly resolved into a mixture of cupric and cuprous oxide, and must therefore be kept under water. It has not yet been obtained quite free from stannous oxide. Dilute hydrochloric acid quickly converts it into a darker coloured substance, probably the corresponding chloride, which is rapidly resolved into metallic copper and cuprous chloride. With hydrogen sulphide it forms a black substance, probably tetracupric sulphide, which when left in the liquid is gradually converted into a higher sulphide, with disengagement of hydrogen. With hydrocyanic acid it yields a black cyanide, which is converted by silver nitrate into silver cyanide, metallic copper, and cupric nitrate (H. Rose, *Pogg. Ann.* cxx. 1; *Jahresb.* 1863, p. 271).

Oxychlorides.—By boiling cupric chloride with a small quantity of potassium or sodium hypochlorite, the oxychloride $CuCl^2.3CuO$ is precipitated in combination with 4 or 6 mol. H^2O, according to the duration of the boiling. The composition of atacamite from Cobija, as determined by Berthier, agrees nearly with the formula $CuCl^2.3CuO + 6H^2O$ (Field, *Phil. Mag.* [4] xxiv. 123). The same oxychloride is precipitated with $3\frac{1}{2}$ mol. water, or as $2(CuCl^2.3CuO) + 7H^2O$, on mixing a hot dilute solution of cupric chloride with a soluble salt of formic, acetic, propionic, or valeric acid: *e.g.* with sodium acetate:

$$4CuCl^2 + 6C^2H^3O^2Na + 3H^2O = CuCl^2.3CuO + 6NaCl + 6C^2H^4O^2;$$

also by mixing a soluble chloride with cupric acetate; with boiling solutions the precipitation takes place immediately; with cold solutions after 24 hours. This hydrated oxychloride is very sparingly soluble; a solution containing only $\frac{1}{25000}$ pt. of anhydrous sodium acetate produces a perceptible turbidity in a solution of cupric chloride. It is of greenish colour, and at first of flocculent consistence; afterwards however it becomes more finely divided and requires the addition of sodium sulphate to separate it from the liquid. It appears to be gradually decomposed by water; when boiled with water it quickly assumes the colour of cupric hydrate (Casselmann, *Zeitschr. anal. Chem.* iv. 34; *Jahresb.* 1865, p. 275).

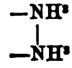
Basic sulphates and nitrates of copper of analogous composition are obtained in like manner, *e.g.* the sulphate $2(SO^4Cu.3CuO).7H^2O$ by mixing a hot dilute solution of cupric sulphate with the soluble salt of a fatty acid, or the copper salt of one of these acids with a soluble sulphate (Casselmann).

A cupric oxychloride having nearly the composition of atacamite, $2(CuCl^2.3CuO) + 9H^2O$, is obtained by boiling precipitated cupric oxide with ammonium chloride. The same oxide boiled for some time with ammonium sulphate yields an apple-green powder consisting of a basic sulphate having nearly the composition of brochantite; with ammonium carbonate, a green carbonate nearly allied to malachite; with ammonium nitrate, a basic cupric nitrate having nearly the composition $2(6CuO.N^2O^5) + 15H^2O$ (Tüttschew, *Zeitschr. f. Chem.* [2] vi. 109).

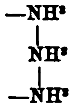
Phosphides (Abel, *Chem. Soc. J.* [2] iii. 249).—Dicupric phosphide, Cu^2P^2, is converted into hexcupric phosphide, Cu^6P^2, by ignition, either alone or in hydrogen gas—in the latter case with evolution of phosphorus vapour and hydrogen phosphide. The hexcupric phosphide, which contains 14 p. c. phosphorus, is the highest phosphide of copper that can exist at a red heat. Phosphorus vapour passed over copper heated to low redness forms, with incandescence, a fused mass which becomes steel-grey and partly crystalline on cooling, contains 12·2 to 13·5 p. c. phosphorus, and does not give off any of it when heated in a tube. By adding phosphorus to fused copper and stirring the mass till it is nearly cold, a product is obtained consisting of three layers, the uppermost being white, very hard, and brittle, with shining crystalline fracture, and containing from 7 to 12 p. c. phosphorus; the middle layer, which forms the principal portion of the mass, being grey, with granular fracture, and containing 4 to 6 p. c. phosphorus; while the lowest, which is insignificant in quantity, consists of nearly pure copper containing only 0·5 p. c. phosphorus.

By adding phosphorus to copper melted at such a temperature that part of it still remains solid, a compound is formed containing from 2 to 4·7 p. c. phosphorus, which by casting in iron moulds may be obtained in homogeneous hard masses having a fine-grained fracture, like that of bell-metal, but quickly tarnishing. By fusing this compound with pure copper, other compounds containing smaller proportions of phosphorus were obtained, which exhibited greater tenacity than ordinary gun-metal: thus the tenacity of the compound containing 2·5 p. c. phosphorus was represented by a breaking power of 47,908 lb. to the square inch, that of gun-metal being from 24,991 to 26,424 lb. The mode of casting has however considerable influence on the physical properties of these phosphoretted coppers: thus copper containing 1 p. c. phosphorus, when cast in an iron mould, exhibited a tenacity of 36·893 lb. to the square inch, whereas when cast in a sand mould, its tenacity was only 13,959 lb. to the square inch. Altogether phosphoretted copper is not adapted for casting, as it contracts very much in solidifying, and when it is cast in moulds of sand or loam, the casting is also porous. By fusing the phosphoretted copper with iron, the greater part of the phosphorus is removed, with formation of iron phosphide, which separates as a distinct layer, while the copper becomes alloyed with iron.

COPPER BASES, AMMONIACAL (i. 79). The ammoniacal cupric compounds consist of a cupric salt, CuR^2 or CuR'', united with the elements of 1, 2, 3, 4, 5, or 6 molecules of ammonia, NH^3. There are also cuprous salts of similar constitution whose formulæ may be derived from the preceding by substitution of $(Cu^2)''$ for Cu''. To explain the constitution of these salts, it must be observed: (1) That NH^3 being a bivalent radicle, any number of such groups united together will also form bivalent radicles; thus:



$$\begin{array}{c} —NH^3 \\ | \\ —NH^3 \end{array}$$



$$\begin{array}{c} —NH^3 \\ | \\ NH^3 \\ | \\ —NH^3 \end{array}$$

(2) The polyammoniacal compounds, when heated, readily give off part of their ammonia, leaving a compound containing $2NH^3$ or $1NH^3$ to one atom of copper, the last atom, NH^3, being moreover retained much more forcibly than any of the rest. Thus the sulphate $5NH^3.SO^4Cu$ heated not quite to 149° gives off $3NH^3$, leaving the compound $2NH^3.SO^4Cu$; and at a little above this temperature it leaves $NH^3.SO^4Cu$, which again at a still higher temperature suffers complete decomposition, giving off nitrogen and other volatile products and leaving metallic copper. The last molecule of ammonia may be supposed to be united with the copper in such a manner as to form the bivalent radicle cuprammonium:

$$\begin{array}{l} —N—Cu— \\ \;\,||| \\ \;\,H^3 \end{array} \qquad \text{or} \qquad (NH^2Cu'')'',$$

which again may unite with other molecules of ammonia, forming other bivalent radicles, $(NH^3—NH^2Cu)''$, $(NH^3—NH^3—NH^2Cu)''$ or $(2NH^3.Cu)''$, $(3NH^3.Cu)''$, &c. Thus we have the following ammonio-cupric chlorides:

$$(NH^2Cu)''Cl^2;\ (2NH^3.Cu)''Cl^2;\ (3NH^3.Cu)''Cl^2;\ (4NH^3.Cu)''Cl^2;$$

also the ammonio-cuprous chlorides:

$$(NH^2Cu^2)''Cl^2;\ (2NH^3.Cu^2)''Cl^2;\ (4NH^3.Cu^2)''Cl^2.$$

All these ammoniacal copper salts are capable of taking up a quantity of oxacid or hydracid sufficient to saturate the ammonia contained in them: thus $NH^3.CuCl^2$ can take up HCl; $4NH^3.CuCl^2$ can take up 4HCl, &c.; but the compounds thus formed are not ammonio-compounds like those above formulated, but true double salts, identical in properties with those formed by the direct union of an ordinary ammonium salt with a cupric salt; thus

$$\begin{aligned} NH^3.CuCl^2 + HCl &= NH^4Cl.CuCl^2. \\ 2NH^3.CuCl^2 + 2HCl &= 2NH^4Cl.CuCl^2. \\ 4NH^3.CuCl^2 + 4HCl &= 4NH^4Cl.CuCl^2. \end{aligned}$$

Under certain circumstances the ammonio-copper compounds can dissolve in water without decomposition, especially at low temperatures or in presence of free ammonia: thus the compound $5NH^3.CuBr^2$ dissolves completely in a small quantity of water and may be crystallised therefrom; but on adding more water, the liquid becomes turbid and deposits cupric hydrate (ii. 52).

CORIAMYRTIN. $C^{30}H^{36}O^{10}$.—The active principle of *Coriaria myrtifolia.* (See Additions, vol. v. p. 1090.)

CORK. This substance has been examined by Siewert (*Zeitschr. f. Chem.* [2] iv. 383) with the following results: 12 pounds of rasped cork were twice boiled in portions of 100 grams each with 4 litres of alcohol of 95° Tr., whereby 10 p. c. of the cork was dissolved. The residue yielded scarcely perceptible traces of substance to alcohol, ether, chloroform, or benzol.

The alcoholic extract first deposited from 1·62 to 1·75 p. c. of Chevreul's cerin (i. 830), as a white, crystalline, neutral substance, together with white masses of an acid compound.—1. Cerin, $C^{17}H^{28}O$, is regarded by Siewert as a homologue of phenol, and designated as phellyl alcohol. It melts at 100°, dissolves in 500 pts. of boiling and 5,000 pts. of cold absolute alcohol.—2. The amorphous acid, called decacrylic acid, has the composition $C^{10}H^{8}O^{2}$. It has an acid reaction; dissolves in 1,200 pts. of cold and 52 pts. of boiling alcohol; melts at 86°; dissolves slowly in aqueous or alcoholic potash at the boiling heat; and separates therefrom as a yellow precipitate on cooling.—3. After the separation of those two substances, the alcoholic extract yielded, on further evaporation, 2·5 p. c. of a fatty substance, eulysin, $C^{24}H^{36}O^{3}$, soluble in 10 pts. of cold alcohol, and melting without decomposition at 150°. —4. The remainder of the alcoholic solution evaporated to dryness left a mass which when repeatedly boiled with water, yielded to that liquid a tannic acid, separating from the aqueous solution in dark red flocks (0·5 p. c.). Its solution forms with gelatin a yellow, with tartar-emetic a brown precipitate, and reduces an ammoniacal silver solution in the cold. Potash and ammonia colour its solution red; baryta-water forms a dark-coloured precipitate. The calcium salt of this acid contains $(C^{27}H^{21}O^{17})^{2}Ca + 8H^{2}O$.—5. The aqueous extract when further evaporated deposited a brown-red precipitate, $C^{12}H^{10}O^{6}$, called by Siewert corticic acid. —6. The portion insoluble in water of the residue obtained by evaporating the original alcoholic extract, had nearly the appearance of the original cork-substance, dissolved easily and almost completely in boiling alcohol, and partly separated on cooling as a jelly (2·5 p. c.). Its alcoholic solution evaporated on paper penetrates the paper like fat.

CORPUS LUTEUM. The yellow particles occurring in the ovary of the cow at a certain stage of development have been examined by Holm (*J. pr. Chem.* c. 142; *Jahresb.* 1867, p. 779) and by Piccolo a. Lieben (*Zeitschr. f. Chem.* [2] iv. 645). The latter evaporated the yellow ethereal extract of these bodies and boiled the residue with potash to saponify the fats. On adding an excess of water, a turbid liquid was obtained, holding in suspension small shining dichroïc crystals. The liquid filtered from these crystals was found to contain cholesterin, together with smaller quantities of one or more amorphous bodies, insoluble in water, but soluble in alcohol, ether, and carbon bisulphide.

The dichroïc crystals are insoluble in water and in alcohol, not attacked by strong potash-ley even at the boiling heat, soluble with yellow colour in ether and in benzol, dissolving very easily in carbon bisulphide with deep red colour, and in chloroform with deep yellow colour. From all these solutions they may be repeatedly recrystallised. Treated with strong sulphuric acid under the microscope, they are seen to turn blue and dissolve. With nitric or hydrochloric acid, they acquire a dark colour soon changing to light yellow. Hydriodic acid turns them brown. They are not altered by sulphurous acid, solution of stannous chloride, or tincture of iodine. Glacial acetic acid does not act on them at ordinary temperatures, but decomposes them when heated. When exposed to the air they gradually lose their deep red colour, more quickly in the light than in the dark. When protected from the air, they remained unaltered for more than a year.

Holm regards these dichroïc crystals as identical with hæmatoïdin; but according to Piccolo a. Lieben, they constitute a distinct substance, which these chemists designate as leuco-haematoïdin or haemoluteïn.

CORUNDOPHILITE. This mineral, occurring at Chester, Massachusetts, has been shown to be identical with clinochlore (*Jahresb.* 1865, p. 893; 1866, p. 936; 1867, p. 993).

CORYDALINE. $C^{18}H^{19}NO^{4}$.—This base, occurring in the roots of *Corydalis bulbosa*, *C. fabacea*, and *Bulbocapnus cavus* (rad. *Aristolochiæ cavæ*), has been further examined by H. Wicke (*Ann. Ch. Pharm.* cxxxvii. 274). To prepare it, the chopped roots of the last-mentioned plant were repeatedly exhausted at 50° with 6 pts. of water containing sulphuric acid; the expressed liquids were precipitated with basic lead acetate; and the filtrate, freed from lead by sulphuric acid, was mixed with metatungstate or phosphotungstate of sodium, in such proportion as to leave the liquid acid. The resulting yellowish-white precipitate was pressed, mixed with levigated chalk, and dried, and the dry mass was exhausted with hot alcohol. On distilling off the alcohol, the corydaline crystallised from the viscid residue in stellate groups of prisms, which were freed from adhering resin by washing with alcohol containing ether, pressing, and recrystallisation from ether-alcohol.

Corydaline crystallises from strong solutions in short prisms, from dilute solutions in slender needles; it is soluble in alcohol, ether, chloroform, amylic alcohol, carbon bisulphide, benzol, and oil of turpentine, but not in water. The alcoholic solution, if free from resin, remains colourless when heated; it has a bitter taste and strong alkaline reaction, and on addition of water deposits the base in microscopic needles. Corydaline melts at 130°, without loss of weight, to a brown-red amorphous mass which solidifies again in the crystalline form after long standing. The alcoholic solution yields a flocculent precipitate with tannic acid; the solution in acids forms precipitates with caustic and carbonated alkalis (soluble in excess of caustic alkali), also with potassium sulphocyanate, mercuric chloride, potassio-mercuric iodide, iodine, sodium picrate, potassium chromate, sodium metatungstate, auric chloride, and platinic chloride.

Corydaline dissolves in *nitric acid*, leaving a brown-red resin. The *hydrochloride* $C^{18}H^{19}NO^4.HCl + 5H^2O$, formed by agitating a solution of corydaline in carbon bisulphide with weak hydrochloric acid, crystallises in tufts of needles which give off all their water over sulphuric acid; from warm dilute hydrochloric acid, the salt separates in the crystalline state. The *platinochloride* $(C^{18}H^{19}NO^4)^2.2HCl.PtCl^4$ is a yellow crystalline precipitate. The *acid sulphate* $C^{18}H^{19}NO^4.H^2SO^4$ forms needle-shaped crystals which dissolve but slowly in water.

Ethyl-corydaline hydriodide, $C^{18}H^{18}(C^2H^5)NO^4.HI$, is formed by heating corydaline to 100° with ethyl iodide, and separates from the yellow solution in reddish-yellow crystals sparingly soluble in water. With moist silver oxide it yields an alkaline solution from which the base cannot be obtained pure. The *platinochloride* $2C^{18}H^{19}(C^2H^5)NO^4Cl.PtCl^4$ is a dingy yellow amorphous precipitate.

COUMARILIC ACID. $C^9H^6O^3$ (Perkin, *Chem. Soc. J.* [2] ix. 45).—The potassium salt of this acid is produced by boiling α-bromocoumarin (p. 499) with potash; and this salt decomposed by hydrochloric acid, yields the acid as a snow-white crystalline precipitate, melting at 192°–193°, subliming when gently heated, and decomposing partially when distilled. The acid is extremely soluble in alcohol, sparingly in chloroform and carbon bisulphide, moderately soluble in boiling water, from which it crystallises in long needles. Not decomposed by heating with potassium hydrate to 180°. It is monobasic, forming easily soluble crystalline salts with ammonia and the alkali metals. The barium, calcium, silver, lead, mercurous, and ferric salts are obtained by precipitation.

Bromocoumarilic acid, $C^9H^5BrO^3$, is formed by decomposing α-dibromocoumarin with potash, and crystallises from weak spirit in needles melting at 250°, having a bitter taste, very soluble in alcohol, sparingly in water. Heated to 180° with potassium hydrate it decomposes and turns brown, with formation of potassium bromide. It is monobasic; the ammonium, potassium, and sodium salts are soluble and crystalline; the barium, silver, and lead salts are white precipitates.

COUMARIN, $C^9H^6O^2$, and **COUMARIC ACID**, $C^9H^8O^3$ (Perkin, *Chem. Soc. J.* [2] vi. 53).—The intimate relation of these bodies to the salicylic series, shown by the conversion of coumaric acid into salicylic and acetic acids by fusion with potash (ii. 93), is further demonstrated by the following mode of formation of coumarin from salicylol. Sodium-salicylol, $C^7H^5NaO^2$ (salicylite of sodium, v. 169), dissolves in acetic anhydride with considerable evolution of heat; and on boiling the solution for a few minutes, and then pouring it into water, an oily body separates, while sodium acetate passes into solution. On distilling this oil, acetic anhydride first passes over, then salicylol, and finally at 290°, a body which crystallises in the receiver, and after repeated crystallisation from alcohol, exhibits the composition and all the properties of coumarin from Tonka beans, melting at 67° to 67·5°, and boiling at 290·5° to 291°.* Its formation may be represented by the following equations:

$$\underset{\text{Sodium-salicylol.}}{C^6H^4\left\{\begin{matrix}ONa\\COH\end{matrix}\right.} + \underset{\substack{\text{Acetic}\\\text{anhydride.}}}{(C^2H^3O)^2O} = \underset{\substack{\text{Sodium}\\\text{acetate.}}}{C^2H^3O.ONa} + \underset{\substack{\text{Acetyl-}\\\text{salicylol.}}}{C^6H^4\left\{\begin{matrix}O(C^2H^3O)\\COH\end{matrix}\right.}$$

and

$$\underset{\text{Acetyl-salicylol.}}{C^6H^4\left\{\begin{matrix}OC^2H^3O\\COH\end{matrix}\right.} - H^2O = \underset{\text{Coumarin.}}{C^6H^3\left\{\begin{matrix}C^2H^3O\\CO\end{matrix}\right.}$$

According to this view, coumarin is a mixed acid radicle composed of acetyl and diptyl, C^7H^3O, a radicle belonging to the cinnamyl series; and in its formation from acetosalicylol, an atom of hydrogen is taken from the benzene residue, C^6H^4, and an atom of oxygen from the group OC^2H^3O.

But the formation of coumarin in this reaction cannot be attributed to the dehydration of acetyl-salicylol by acetic anhydride; for these two bodies when heated together to 150° unite and form a definite compound, $C^9H^8O^3.C^4H^6O^3$, which is resolved by distillation into its original components. Moreover, acetic anhydride and acetosalicylol may be distilled together at higher temperatures without yielding a trace of coumarin. The formation of coumarin in the action of acetic anhydride on sodium-salicylol, as above described, depends indeed on the simultaneous formation of sodium acetate; for when a mixture of acetyl-salicylol, acetic anhydride, and sodium acetate is heated to the boiling point, a considerable quantity of coumarin is produced. Perkin attributes the influence of the sodium acetate in this reaction to the formation of a compound of that salt with acetic anhydride, like the anhydro-diacetate of potassium (i. 18); but it is by no means obvious why such a compound should exert a stronger dehydrating action than acetic anhydride itself (Perkin, *Chem. Soc. J.* [2] vi. 181).

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* Perkin finds that the melting and boiling points of natural coumarin are about 20° higher than those hitherto assigned to it.

According to Fittig, on the other hand (*Zeitschr. f. Chem.* [2] iv. 595), the product of the reaction of acetic anhydride on sodium-salicylol at high temperatures is not acetyl-salicylol, but its isomeride, coumaric acid, the reaction being analogous to that by which cinnamic acid is formed from acetyl chloride and benzoic aldehyde (i. 983); in fact, coumaric acid bears to cinnamic acid the same relation as salicylol to benzoic aldehyde; thus:

C^7H^6O	+	C^2H^3OCl	=	HCl	+	$C^9H^8O^2$
Benzoic aldehyde.		Acetyl chloride.				Cinnamic acid.
$C^7H^6O^2$	+	C^2H^3OCl	=	HCl	+	$C^9H^8O^3$
Salicylol.		Acetyl chloride.				Coumaric acid.
$C^7H^5O^2Na$	+	$(C^2H^3O)^2O$	=	$C^2H^3O^2Na$	+	$C^9H^8O^3$
Sodium-salicylol.		Acetic anhydride.		Sodium acetate.		Coumaric acid.

The coumaric acid, at the high temperature at which it is formed, is then resolved into coumarin and water.

According to these views, coumarin is the anhydride of coumaric acid. But it does not appear to be producible from coumaric acid by the action of any of the ordinary dehydrating agents; moreover, as pointed out by Perkin, it is formed in plants in presence of water, and may be repeatedly crystallised from water without alteration. When boiled with strong potash-ley it yields a saline compound, from which it is separated by acids still as coumarin, and to convert it into coumaric acid it required to be boiled with a supersaturated solution of caustic alkali. Again, coumarin does not form an amide with ammonia as true anhydrides do (Perkin, *Chem. Soc. J.* [2] vii. 192). See further Bäsecke (*Zeitschr. f. Chem.* [2] iv. 585).

When sodium-amalgam is added by small portions to a solution of coumarin in water containing a little alcohol, at 40°-60°, the coumarin is first converted, by assumption of water, into coumaric acid, and this, by addition of hydrogen, is transformed into melilotic or hydrocoumaric acid, $C^9H^{10}O^3$ (Zwenger, *Jahresb.* 1865, p. 343; 1867, p. 443).

The coumarin of *Melilotus officinalis* is in combination with melilotic acid. When the evaporated aqueous decoction of the plant is treated with ether, as long as the ether acquires an acid reaction, and the green mass remaining after evaporation of the ether is repeatedly boiled with a large quantity of water, a solution is obtained, which on cooling deposits large well-defined crystals of the compound of coumarin with melilotic acid, while free melilotic acid remains in solution. The crystals, after repeated crystallisation from alcohol, with addition of animal charcoal, are colourless, apparently rhomboidal plates, or silky needles. They have an aromatic bitter taste, smell like coumarin when heated, dissolve sparingly in cold, more easily in boiling water, very easily in alcohol and ether. Ammonia decomposes them in the cold, dissolving the melilotic acid, and separating coumarin identical in every respect with that obtained from Tonka beans (Zwenger a. Bodenbender, *Ann. Ch. Pharm.* cxxvi. 257; *Jahresb.* 1863, p. 552).

COUMARIN DIBROMIDE, $C^9H^6O^2Br^2$, isomeric with dibromomelilotic anhydride, is formed by adding about 7 pts. of powdered coumarin to 8 pts. of bromine, both dissolved in carbon bisulphide. On leaving the solution to itself for about twelve hours, and then evaporating the solvent, a crystalline mass is obtained, which may be freed from secondary products by washing with a little cold alcohol and recrystallisation from the same solvent, with the aid of but little heat. The dibromide crystallises in transparent oblique prisms, melting at about 100°, with partial decomposition, and giving off bromine at a higher temperature. It dissolves easily in alcohol, and decomposes quickly when boiled with alcohol or when its alcoholic solution is exposed to light, the bromine apparently acting on the solvent, and leaving coumarin in solution (Perkin, *Chem. Soc. J.* [2] viii. 368; ix. 37).

BROMCOUMARINS.—Mono- and di-bromocoumarin have been obtained, each in two modifications. *a-Monobromocoumarin*, $C^9H^5BrO^2$, is most easily prepared by decomposing the dibromide of coumarin with alcoholic potash. It crystallises from alcohol in transparent needles about half an inch long, melting at 110°. Heated to 200° in a sealed tube for five or six hours, it decomposes slightly, with formation of hydrobromic acid. Cold alcoholic ammonia decomposes it, with formation of ammonium bromide and a glutinous substance soluble in water. Heated with potassium hydrate, it yields bromide and coumarilate of potassium.—*β-Monobromocoumarin* is formed by the action of acetic anhydride on sodium bromosalicylol. On boiling the product for ten or fifteen minutes and pouring it into water, the β-bromocoumarin separates as a heavy oil which, when purified by rectification, boils at 160°. When boiled with alcoholic or aqueous potash, it does not decompose, but simply dissolves like ordinary coumarin (Perkin, *loc. cit.*).

α-Dibromocoumarin, $C^9H^4Br^2O^2$, is prepared by heating a mixture of 1 pt. coumarin, 2 pts. bromine, and 4 or 5 pts. carbon bisulphide, with addition of iodine, in a bath of salt and water for four or five hours. The product is freed from carbon bisulphide by evaporation, from iodine by means of potassium iodide, and finally purified by two or three crystallisations from alcohol. It crystallises in small needles melting at about 183°; is easily decomposed by alcoholic potash, yielding potassium bromide and the potassium salt of a new acid; and by alcoholic ammonia, with formation of ammonium bromide and a crystalline product.—*β-Dibromocoumarin*, $C^9H^4Br^2O^2$, obtained by the action of acetic anhydride on sodium-dibromosalicylol, crystallises in hard needles melting at 176° and not decomposed by alcoholic potash (Perkin).

COUMARIN DICHLORIDE, $C^9H^6O^2.Cl^2$, is produced by direct combination when chlorine is passed into a solution of coumarin in chloroform, and remains on leaving the solution to evaporate, as a syrupy product having the appearance of new honey. It is converted by distillation into chlorocoumarin, and is decomposed by alcoholic potash, like the dibromide (Perkin, *Chem. Soc. J.* [2] ix. 43).

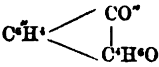
CHLOROCOUMARINS.—*α-Chlorocoumarin*, $C^9H^5ClO^2$, is produced by heating a mixture of 1 pt. coumarin and 3 pts. phosphorus pentachloride to about 200°, or more easily by treating the dichloride with alcoholic potash. It crystallises in flat needles, moderately soluble in alcohol, slightly in hot water, melting at 122°–123°, emitting an aromatic odour when heated, and resolved by boiling with alcoholic potash into hydrobromic and coumarilic acids (Perkin).

β-Chlorocoumarin, $C^9H^5ClO^2$, is obtained by the action of acetic anhydride on sodium-chlorosalicylol. It crystallises in needles, melting at 162°, subliming even below that temperature, nearly insoluble in cold, perceptibly soluble in boiling water, slightly soluble in cold alcohol and ether, very soluble in benzol and carbon bisulphide. Potash at a gentle heat dissolves it without alteration, but by prolonged boiling with strong potash-ley it is converted into chlorocoumaric acid, and by fusion with potassium hydrate into chlorosalicylic acid (Bäsecke, *Ann. Ch. Pharm.* cliv. 84; *Zeitschr. f. Chem.* vi. 583).

Tetrachlorocoumarin, $C^9H^2Cl^4O^2$, is formed by passing chlorine into a solution of coumarin and iodine in carbon tetrachloride. It crystallises from alcohol in small white needles melting at 144°–145°, and is decomposed by heating with alcoholic potash into hydrobromic acid and a new acid not yet examined (Perkin).

Homologues of Coumarin and Coumaric Acid (Perkin, *Chem. Soc. J.* [2] vi. 53, 472).—Compounds homologous with coumarin are obtained by the action of butyric and valeric anhydrides on sodium-salicylol, the mode of action being exactly similar to that by which coumarin itself (acetic coumarin) is formed.

BUTYRIC COUMARIN. $C^{11}H^{10}O^2 = \overset{'''}{C^6}H^3\left\{\begin{matrix}CO''\\C^4H^7O\end{matrix}\right.$ or



$\overset{''}{C^6}H^4\left\langle\begin{matrix}CO''\\|\\C^4H^6O''\end{matrix}\right.$.—Produced by heating sodium-salicylol with butyric anhydride, boiling the product for a few minutes, then pouring it into water, distilling the oil which separates, and collecting the portion which passes above 290°. It melts at 70°–71°, solidifies to a crystalline mass on cooling, and distils, with slight decomposition, at 296°–297°. It dissolves sparingly in boiling water, easily in alcohol and ether. The aqueous solution becomes turbid on cooling, and deposits a few needle-shaped crystals; from alcohol the compound crystallises in large translucent prisms. It smells like ordinary coumarin, and at the same time like fresh honey. It is nearly insoluble in strong aqueous potash at ordinary temperatures, but when heated with it, forms a pale yellow solution, which on evaporation deposits a deliquescent potassic compound of butyric coumarin (*infra*). By fusion with potash, butyric coumarin yields salicylic acid, phenol, and apparently also butyric acid. With bromine it reacts like ordinary coumarin, becoming liquid, and yielding on subsequent distillation a resinous mass, which when heated with alcoholic potash, forms an acid separable by hydrochloric acid.

VALERIC COUMARIN. $C^{12}H^{12}O^2 = \overset{'''}{C^6}H^3\left\{\begin{matrix}CO''\\C^5H^9O\end{matrix}\right.$ or $\overset{''}{C^6}H^4 \left\langle\begin{matrix}CO''\\ | \\ C^5H^8O''\end{matrix}\right.$.—Prepared by adding sodium-salicylol by small portions to boiling valeric anhydride, distilling the oil separated by water, collecting the portion which distils above 290°, dissolving it in strong boiling potash-ley, agitating the diluted solution with ether to remove oily products, and decomposing the clear aqueous solution with hydrochloric acid. The compound thereby separated is dissolved in ether; the ethereal solution, after agitation with sodium carbonate, is evaporated; and the residual oil, which solidifies to a crystalline mass, is pressed between bibulous paper and several times recrystallised from alcohol. The product thus obtained is pure valeric coumarin; it melts at 54°, boils with slight decomposition at 301°, smells like coumarin, but less strongly than the preceding compound, is nearly insoluble in cold water, and crystallises from alcohol in transparent prisms nearly ¾ inch long. With potash-ley and solid potassium hydrate it reacts like butyric coumarin.

BUTYRO-COUMARIC ACID. $C^{11}H^{12}O^3 = C^6H^4\left\{\begin{matrix}C^4H^7O\\COOH\end{matrix}\right.$.—This acid is formed from butyric coumarin in the same manner as coumaric acid from coumarin. Butyric coumarin dissolves in boiling aqueous potash, and on evaporating the solution, an oily layer separates, which solidifies on cooling to a hard mass consisting of a compound of 1 mol. butyric coumarin with 1 mol. potassium hydrate. This compound when heated melts, boils up, becomes pasty and frothy, and is converted into a soft mass perfectly soluble in water; and on adding hydrochloric acid to this solution, butyro-coumaric acid separates as a white crystalline mass, which may be purified by solution in ammonia and reprecipitation with hydrochloric acid, and finally by digestion with chloroform, which removes traces of unaltered butyric coumarin. Butyro-coumaric acid crystallises in flat shining prisms, melting with slight decomposition at 174°. It is extremely soluble in alcohol and ether, sparingly soluble in water and in chloroform, and does not exhibit any coloured reaction with iron salts. Its *sodium salt* is crystalline and very soluble. The solution of the *ammonium salt* leaves the acid when evaporated. The *silver salt* $C^{11}H^{11}O^3Ag$ is a light yellow precipitate, becoming white and crystalline after a short time; it is somewhat soluble in water and blackens at 100° (Perkin).

CREATINE. $C^4H^9N^3O^2$.—From the decomposition of creatine by baryta-water into urea and sarcosine (methyl-glycocine) Strecker inferred that it is a compound of cyanamide (urea minus water) with methyl-glycocine (ii. 98):

$$\underset{\text{Cyanamide.}}{\left.\begin{matrix}CN\\H^2\end{matrix}\right\}N} \quad + \quad \underset{\text{Methyl-glycocine.}}{\left.\begin{matrix}(C^2H^2O)''\\CH^3\\H^2\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}} \quad = \quad \underset{\text{Creatine.}}{\left.\begin{matrix}CN\\(C^2H^2O)''\\CH^3\\H^4\end{matrix}\right\}\begin{matrix}N^3\\O\end{matrix}}$$

In corroboration of this view, Volhard (*Zeitschr. f. Chem.* [2] v. 319) has lately produced creatine by direct union of cyanamide and sarcosine. The combination may be effected by heating the two bodies together in alcoholic solution to 100° for some hours, or by mixing them in aqueous solution, and either evaporating or leaving the liquid to itself for some time. In either case creatine crystallises out mixed with more or less creatinine formed from it by the action of heat. Strecker some years ago obtained glycocyamine, $C^3H^7N^3O^2$, the lower homologue of creatine, by combining cyanamide with glycocine (ii. 906).

The following method of estimating the amount of creatine in muscular flesh is given by Neubauer (*Zeitschr. anal. Chem.* ii. 22). From 200 to 250 grms. of finely chopped meat is heated to 55°–60° with an equal weight of water for ten or fifteen minutes, with constant stirring, till the albumin begins to coagulate. The liquid is thoroughly expressed, the residue being twice stirred up with 60 to 80 c.c. water; heated over the open fire till the albumin is completely coagulated; filtered when cold; precipitated with basic lead acetate, carefully avoiding an excess; and the solution, freed from lead by hydrogen sulphide, is finally evaporated over the water-bath to a thin syrup. The colourless creatine which is deposited after a few days is separated from the mother-liquor; the latter is mixed with 2 to 3 vol. strong alcohol; and the entire crystalline mass (after washing with alcohol of 88 p. c. and finally with absolute alcohol) is collected on a small weighed filter, dried at 100°, and weighed. As creatine gives off 12·17 p. c. water at 100°, this water must be taken into account in estimating the amount of crystallised creatine. By this method, Neubauer has found the amount of creatine in 100 pts. of the flesh of various animals to be as follows:

	Ox			Pig		Calf	Sheep	
	1	2	3	1	2		1	2
Creatine dried at 100°	0·150	0·204	0·193	0·117	0·184	0·160	0·157	0·166
„ crystallised	0·170	0·232	0·220	0·133	0·209	0·182	0·179	0·189

No creatinine was found either in the creatine thus prepared, or in the mother-liquor from which it had crystallised. Hence, and from the fact that creatine is converted into creatinine by prolonged heating, Neubauer concludes that creatinine is altogether absent from normal muscular flesh, that consequently in the metamorphosis of tissue creatine is the primary product; and that this substance in its passage through the blood is converted by the action of heat into creatinine, which is eliminated in the urine.

Nawrocki also (*Zeitschr. anal. Chem.* iv. 330) concludes from experiments on frogs, that the muscles (whether at rest or tetanised) contain no creatinine, and that the quantity of creatine in frogs' muscles (0·221 to 0·388 p. c.) does not diminish during muscular activity.

Creatine may be conveniently prepared from Liebig's extract of meat, in which it occurs crystallised, together with a small quantity of creatinine. To obtain it, 40 pts. by weight of the extract are dissolved in 800 pts. of water; the solution is precipitated with a slight excess of basic lead acetate, filtered, and freed from lead by hydrogen sulphide; the liquid again filtered is evaporated down to 40 pts. (the original weight); and the creatine deposited from this concentrated liquid is collected on a filter and washed. The mother-liquor, after standing for a week, deposits an additional quantity (Mulder a. Mouthaan, *Zeitschr. f. Chem.* [2] v. 341).

A concentrated aqueous solution of *cadmium chloride* saturated at 50° with creatine, deposits, first unaltered creatine, then by evaporation over sulphuric acid, a compound of creatine with cadmium chloride, $C^4H^9N^3O^2.CdCl^2.2H^2O$, in large colourless crystals, which give off their water at 100° and are resolved by hot water into creatine and cadmium chloride. In the same manner may be obtained a compound of creatine with *zinc chloride*, $C^4H^9N^3O^2.ZnCl^2$, in small anhydrous crystals, which are likewise decomposed by hot water. Creatine forms similar compounds with *cupric chloride* and *mercuric nitrate* (Neubauer, *Ann. Ch. Pharm.* cxxxvii. 298).

CREATININE. $C^4H^7N^3O$.—The whey of milk after putrefaction contains creatinine, evidently produced from the creatine in the fresh whey (Commaille, *Zeitschr. f. Chem.* [2] vi. 93).

Creatinine heated with concentrated *baryta-water* is resolved into ammonia and methyl-hydantoïn (Neubauer, *Ann. Ch. Pharm.* cxxxvii. 288); see HYDANTOÏN:

$$C^4H^7N^3O + H^2O = NH^3 + C^4H^6N^2O^2.$$

Action of Nitrous Acid.—Dessaignes, by passing nitrous acid vapour into a solution of creatinine, obtained, with evolution of carbon dioxide, a base to which he assigned the formula $C^6H^{10}N^6O^3$ (ii. 102). This reaction has been further examined by Märcker (*Ann. Ch. Pharm.* cxxxiii. 305; *Jahresb.* 1865, p. 406), who finds that nitrogen is evolved as well as carbon dioxide, and assigns to the base discovered by Dessaignes the formula $C^4H^8N^4O^2$; he has also shown that a second base isomeric with the first is produced at the same time.

When the nitrous gas evolved from a mixture of arsenious oxide and nitric acid is passed into a concentrated aqueous solution of creatinine, a brisk evolution of carbon dioxide and nitrogen takes place, and the brown liquid deposits well-defined crystals of the nitrate of a base *a*, which by repeated precipitation with ammonia is obtained as a white powder formed of microscopic needles, and having the composition $C^4H^8N^4O^2$. It is but slightly soluble in cold water or alcohol, and quite insoluble in ether. Its *hydrochloride*, $C^4H^8N^4O^2.HCl.H^2O$, crystallises in laminæ or prisms easily soluble in hot water, slightly soluble in strong alcohol, insoluble in ether. The platinum and gold salts of this base cannot be prepared, inasmuch as they are very easily decomposed, with reduction of the metal. The *nitrate* $C^4H^8N^4O^2.HNO^3$ forms large rhombic tables soluble in water, insoluble in alcohol and ether.

The mother-liquor from which the preceding base has been separated by ammonia contains, together with a large quantity of ammonium nitrate, a second base, *β*, isomeric with the first, the nitrate of which separates out on evaporation. This base crystallises from water in spherical nodules, and dissolves easily in water and dilute alcohol, but is insoluble in ether. The *hydrochloride* is likewise easily soluble in cold water and crystallises in white laminæ. The *platinochloride* $2(C^4H^8N^4O^2.HCl).PtCl^4$ is insoluble in ether-alcohol, soluble in water and in alcohol, and crystallises in yellow tables.

The formation of both these bases is represented by the equation:

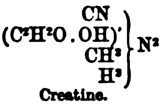
$$2C^4H^7N^3O + 11O = C^4H^8N^4O^2 + 3H^2O + 4CO^2 + N^2.$$

The base α, insoluble in water, melts at 210°, with evolution of gas, and leaves a residue which is resolved by hydrochloric acid into an insoluble brown substance, and the soluble hydrochloride of a base, $C^7H^{12}N^{10}O^2$ (?), precipitated by ammonia in gelatinous flocks. The base β melts at 195°, and carbonises with slight evolution of gas at 220°.

By carefully mixing the base α under water with *bromine*, a non-basic body, $C^4H^7BrN^4O^2$, is formed, easily soluble in water, and crystallising therefrom in yellowish needles; with excess of bromine a brominated resin is produced.

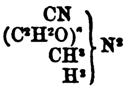
The base α heated to 160° with *ethyl iodide* is converted into a brown syrup which contains a large quantity of free iodine, and is decomposed by boiling with silver oxide, with evolution of ethylamine, and formation of a base, $C^4H^9NO^4$ (?), which crystallises in needles melting at 152°.

Constitution of Creatine and Creatinine.—Allusion has already been made to Strecker's view of the constitution of creatine, according to which it is regarded as a hydoramine containing the elements of cyanamide and methyl-glycocine, and represented by the formula $\left.\begin{matrix}CN\\(C^2H^2O)''\\CH^3\\H^4\end{matrix}\right\}\begin{matrix}N^2\\O\end{matrix}$. By a slight alteration the formula may be converted into that of a diamine containing hydroxyl-glycollyl, $C^2H^2O.OH$, a monatomic radicle, which may be supposed to exist in glycollic acid, $C^2H^2O^2\left\{\begin{matrix}OH\\OH\end{matrix}\right.$; and creatinine, which is derived from creatine by abstraction of the elements of water, may be represented as a diamine containing the diatomic radicle glycollyl, C^2H^2O; thus:



$$\left.\begin{matrix}CN\\(C^2H^2O.OH)'\\CH^3\\H^3\end{matrix}\right\}N^2$$

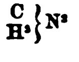
Creatine.



$$\left.\begin{matrix}CN\\(C^2H^2O)''\\CH^3\\H^3\end{matrix}\right\}N^2$$

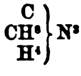
Creatinine.

These two bodies, both of which yield methyl-guanidine (methyluramine) by oxidation, may also be represented as triamines derived from methyl-guanidine; creatine by substitution of hydroxyl-glycollyl for 1 at. hydrogen, creatinine by substitution of glycollyl for 2 at. hydrogen:



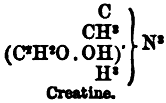
$$\left.\begin{matrix}C\\H^5\end{matrix}\right\}N^3$$

Guanidine.



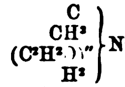
$$\left.\begin{matrix}C\\CH^3\\H^4\end{matrix}\right\}N^3$$

Methyl-guanidine.



$$\left.\begin{matrix}C\\CH^3\\(C^2H^2O.OH)'\\H^3\end{matrix}\right\}N^3$$

Creatine.



$$\left.\begin{matrix}C\\CH^3\\(C^2H^2O)''\\H^2\end{matrix}\right\}N^3$$

Creatinine.

CREOSOL. See the next article.

CREOSOTE (ii. 104). From further experiments by Gorup-Besanez (*Ann. Ch. Pharm.* cxliii. 129; *Jahresb.* 1867, p. 683), it appears that the several varieties of wood-tar creosote are mixtures of compound ethers of guajacol, $C^7H^8O^2$, and creosol, $C^8H^{10}O^2$, the former predominating in Rhenish beech-tar creosote, the latter in Moravian and English creosote. Rhenish creosote has a sp. gr. of 1·0831 at 17·5°, and begins to boil at 130°, but the greater part distils between 199° and 208°, a smaller portion between 208° and 216°, leaving a dark-coloured residue. The portion distilling between 199° and 208° has a sp. gr. of 1·077 at 14°, does not solidify at −11·3°, and when repeatedly distilled does not exhibit any constant boiling point. This distillate dissolves completely in acetic acid of sp. gr. 1·045, also in dilute potash-ley and in excess of aqueous ammonia. Its alcoholic solution mixed with an alcoholic solution of ferric chloride acquires a fine emerald-green colour. This character serves to distinguish wood-creosote from phenol, the alcoholic solution of which forms a brown mixture with alcoholic ferric chloride. According to Ruot (*Bull. Soc. Chim.* [2] viii. 375), a solution of ferric chloride mixed with ammonia till the precipitate just becomes permanent, is coloured blue or violet by phenol, green and afterwards brown by beech-tar creosote. Another distinctive test is afforded by collodion, 15 pts.

phenol and 10 pts. collodion forming a gelatinous mass, whereas creosote forms with collodion a transparent liquid.

When potassium chlorate is added by small portions to a warmed mixture of beech-tar creosote and hydrochloric acid, till green chlorine-vapours begin to escape (for which 18 to 24 hours' treatment is necessary), and the pasty yellow mass obtained on cooling is washed with water and with alcohol, golden-yellow scales are obtained, which when sublimed and treated with cold chloroform are separated into insoluble tetrachloroguajacone, $C^7H^2Cl^4O^2$, and soluble tetrachlorocreosone, $C^8H^4Cl^4O^2$, bodies homologous with a compound having the composition of tetrachloroquinone. Gorup-Besanez supposes them to be formed in the manner represented by the equations:

$$\underset{\text{Guajacol.}}{C^7H^8O^2} + 10Cl = \underset{\substack{\text{Tetrochloro-}\\ \text{guajacone.}}}{C^7H^2Cl^4O^2} + 6HCl.$$

$$\underset{\text{Creosol.}}{C^8H^{10}O^2} + 10Cl = \underset{\substack{\text{Tetrachloro-}\\ \text{creosone.}}}{C^8H^4Cl^4O^2} + 6HCl.$$

For another view of their formation see p. 506. Tetrachloroguajacone and tetrachlorocreosone are lemon-yellow crystalline bodies nearly insoluble in cold water and alcohol, slowly soluble in cold ether, easily soluble in boiling alcohol and chloroform. The former sublimes at 180°, the latter at 160°–170°. Dilute potash-ley colours tetrachloroguajacone blackish-grey or black, tetrachlorocreosone grass-green; warm potash-ley dissolves both with black-brown colour. The bodies formerly described as hexachloroxylin and pentachloroxylin (ii. 105) agree in all their properties, excepting solubility in ether, with tetrachloroguajacone and tetrachlorocreosone, and are regarded by Gorup-Besanez as mixtures of the two with trichlorocreosone, $C^8H^5Cl^3O^2$.

When creosote saturated with water is treated with *phosphorus* and *iodine*, the latter being added by small portions and the phosphorus kept in slight excess, methyl-iodide distils over and a viscid residue is left containing pyrocatechin, together with amorphous phosphorus, and an oil having an intolerable odour. By lixiviating this residue with water, neutralising with barium carbonate, precipitating the filtrate with lead acetate, decomposing the washed precipitate with hydrogen sulphide, evaporating the solution, pressing the crystals thereby obtained, and subliming them, pyrocatechin is obtained with all its characteristic qualities. It is formed from guajacol as represented by the equation:

$$C^7H^8O^2 + HI = CH^3I + C^6H^6O^2$$

(Gorup-Besanez). H. Müller (*Zeitschr. Ch. Pharm.* 1864, p. 40) obtained from English creosote by the same process a syrupy uncrystallisable liquid, $C^7H^8O^2$, which is a homologue of pyrocatechin, and is formed in like manner from creosol, the chief constituent of English wood creosote:

$$C^8H^{10}O^2 + HI = CH^3I + C^7H^8O^2.$$

Gorup-Besanez has lately obtained the same compound, homopyrocatechin, together with a small quantity of pyrocatechin, from a sample of Rhenish beech-tar creosote consisting chiefly of creosol (*Zeitschr. f. Chem.* [2] iv. 393). The same kind of creosote distilled with manganese dioxide and dilute sulphuric acid, yielded phlorol or phloryl alcohol, $C^8H^{10}O$ (Gorup-Besanez and v. Rad, *ibid.* 560).

Lastly, the composition of Rhenish beech-tar creosote has been examined by Marasse (*Deut. chem. Gesellsch.* Berlin, 1868, p. 99; 1869, p. 71; *Zeitschr. f. Chem.* [2] iv. 502; v. 348), who finds that it may be resolved by repeated fractional distillation into three portions, boiling at constant temperatures, the first passing over at 184°, the second between 200° and 203°, the third between 217° and 220°. The portion boiling at 184° solidifies on cooling and consists of phenol. The distillate obtained between 200° and 203° is a mixture of guajacol (boiling at 200°) and cresol, C^7H^8O (boiling at 203°). The third portion, boiling between 217° and 220° (that in which Hlasiwetz, Müller, and Gorup-Besanez had found creosol), was converted, by heating to 150° in a sealed tube with hydriodic acid, into methyl iodide, homopyrocatechin, and phlorol, $C^8H^{10}O$.

Marasse finds that pure guajacol treated with potassium chlorate and hydrochloric acid does not yield a trace of chlorinated quinones; but the portion of beech-tar creosote boiling between 200° and 203° treated in this manner yields the tetrachloroguajacone, $C^7H^2Cl^4O^2$, described by Gorup-Besanez (p. 503), its formation being due to the cresol contained in that portion of the distillate. The occurrence of phlorol in the least volatile portion of the creosote accounts in like manner for the production of tetrachlorocreosone, $C^8H^4Cl^4O^2$, by the action of hydrochloric acid and potassium chlorate, and of phlorone, $C^8H^8O^2$, by that of manganese dioxide and sulphuric acid. The same compound was obtained by Rommier a. Boulhon (*Jahresb.* 1862, p. 322) by the action of manganese dioxide and sulphuric acid on the portion of acid coal-tar oil distilling between 195° and 220°.

From these results it appears that Rhenish beech-tar creosote is a mixture of the following compounds:

Phenol series.	*Guajacol series.*
$C^6H^5.OH$ (B.P. 184°)	$C^6H^4.OCH^3.OH$ (B.P. 200°)
$C^6H^4(CH^3).OH$ (B.P. 203°)	$C^6H^3.CH^3.OCH^3.OH$ (B.P. 217°)
$C^6H^3(CH^3)^2.OH$ (B.P. 220°)	

The existence of phenol in this creosote is confirmed by the experiments of Frisch (*J. pr. Chem.* c. 223; *Jahresb.* 1867, p. 689), who obtained phenylsulphuric acid by treating it with strong sulphuric acid; dinitrophenic and trinitrophenic (picric) acids by subjecting it to the action of strong nitric acid; and several chlorinated quinones and hydroquinones by the action of potassium chlorate and hydrochloric acid.

Creosol. $C^8H^{10}O^2$ (ii. 105).—When rectified creosote is heated for several hours to 60°, with an equal weight of strong sulphuric acid, *creosol-sulphuric* or *sulphocreosolic acid*, $C^8H^{10}SO^5 = C^8H^9O^2.SO^3H$, is formed as a deep red mass which dissolves with violet colour in water. The pure acid separated from its lead salt is obtained by evaporation as a light yellow syrup, which on exposure to the air quickly turns brown and absorbs water. Its salts are crystallisable, easily soluble in water and alcohol. The *potassium salt* $C^8H^9SO^5K$ forms nodular groups of slender needles; the *lead salt* $(C^8H^9SO^5)^2Pb$ dries up in a vacuum to a light yellow mass of slender needles.

Creosyl chloride, C^8H^9OCl, produced by the action of phosphorus pentachloride on rectified creosote, is a limpid, strongly refracting, mobile, oily liquid, having a faint acid reaction, a slightly pungent not unpleasant odour, a very sharp taste, and a sp. gr. of 1·028; it turns brown in the air, dissolves sparingly in water, easily in alcohol and ether. With silver nitrate it forms silver chloride; with ferric chloride it exhibits a fine green, with ammonia a dark brown colour; alkalis abstract the chlorine (Bichele, *Ann. Ch. Pharm.* cli. 104).

When 1½ pt. creosote is heated to 140°–150° with 1 pt. oxalic acid and 2 pts. strong sulphuric acid, carbon dioxide, carbon monoxide, and water are given off, the mass acquires a dark brown-red colour, and after boiling with water, which dissolves a large quantity of phenylsulphuric acid, solidifies to a black-brown brittle resin. This substance is insoluble in water, soluble in glacial acetic acid, sparingly soluble in cold, more easily in boiling alcohol, soluble with splendid purple-red colour in ammonia and potash-ley, and separates therefrom on neutralisation in orange-coloured flocks, which become resinous again when warmed. The compound when dried has a splendid orange-red colour, like that of precipitated alizarin. It melts at 80°, giving off phenol. It becomes colourless when treated with iron-filings and acetic acid, or with sodium-amalgam, but is not affected by alkalis. Its percentage composition is represented by the formula C^5H^4O (Kolbe a. Schmitt, *Ann. Ch. Pharm.* cxix. 169). Wanklyn (*Chem. News*, x. 171) suggests that it may have the constitution $C^2\left\{\begin{matrix}OC^6H^5\\OH\end{matrix}\right.$, formed on the ethylene type.

CRESOL. $C^7H^8O = C^6H^4(OH).CH^3$. *Cresyl Alcohol. Cresylic Phenol.*—This body was first obtained in an impure state from urine by Städeler (1850), who called it *taurylic acid* (v. 701). Williamson and Fairlie (1854) prepared it by fractional distillation from coal-tar creosote, in the form of a liquid boiling constantly at 203°, and Duclos (1859) obtained it from the creosote of fir-wood tar (ii. 106). More recently it has been produced by definite reactions, viz.: 1. By the action of water on nitrate of diazotoluene (Griess, *Jahresb.* 1866, p. 458):

$$C^7H^6N^2 + H^2O = C^7H^8O + N^2.$$

2. By fusing potassium toluene-sulphate with potassium hydrate (Wurtz, *ibid.* 1867, p. 612):

$$C^6H^4(SO^3K).CH^3 + KOH = SO^3K^2 + C^6H^4(OH).CH^3.$$

3. By heating thymol with phosphoric anhydride, whereby the thymol is resolved into cresol and propylene (Engelhardt a. Latschinoff):

$$C^{10}H^{14}O = C^7H^8O + C^3H^6.$$

Now there are two isomeric modifications of toluene-sulphuric acid, α and β, distinguished by the different degrees of solubility of their potassium salts (p. 286), and these when fused with potash yield two isomeric cresols, α and β, one of which (α) is identical with the cresol of coal-tar and wood-tar. The cresol obtained from thymol constitutes a third modification, γ (E. and L.). These three modifications are doubtless the ortho-, meta-, and para-cresols, resulting from the different relative positions of the radicles OH and CH^3; thus:

$C^6H^4(OH).CH^3$ Ortho-cresol. $C^6H^3(OH)H.CH^3$ Meta-cresol. $C^6H^2(OH)H^2.CH^3$. Para-cresol.

PARA-CRESOL is prepared: 1. By fusing the potassium salt of α-toluene-sulphuric acid with 3 pts. potassium hydrate, dissolving the fused mass in water, neutralising with hydrochloric acid, dissolving out the separated cresol with ether, dehydrating the ethereal solution with calcium chloride, evaporating the ether, and distilling the residue in a stream of carbon dioxide.—2. By converting the sulphate of α-toluidine (ordinary crystallised toluidine) into the corresponding salt of diazotoluene (v. 867) by treatment with nitrous acid, and decomposing this salt with boiling water. Cresol obtained by either of these processes has exactly the same properties, and may be completely purified by treating it with benzoyl chloride, recrystallising the resulting benzoyl-cresol from ether, and decomposing it with potash at 100°.

Paracresol thus prepared is a transparent colourless liquid, having a disagreeable phenolic odour like that of putrid urine. It solidifies in a freezing mixture to a lamino-crystalline mass which does not melt again at ordinary temperatures. Boils at 198°–200° (Engelhardt a. Latschinoff). A. v. Rad (*Zeitschr. f. Chem.* [2] v. 715) by treating commercial coal-tar creosote by the process applied by Duclos to wood creosote (ii. 106) finds that the portion of the product boiling at 198° has the composition of cresol, C^7H^8O, whereas the portion boiling at 203° (the boiling point found by Williamson a. Fairlie and by Duclos) contains about 2 p. c. carbon more than the quantity required by the formula of that body. When the cresol thus obtained is very gently heated with potassium chlorate and hydrochloric acid, it is converted, according to v. Rad, into trichlorocresol, which crystallises from hot alcohol in yellow laminæ. Other chemists, however, have obtained by this reaction chlorinated homologues of quinone (p. 503).

Methyl-paracresol or *Methyl-cresylic ether*, $C^7H^7O.CH^3$ or $C^6H^4(OCH^3).CH^3$, is obtained by the action of methyl-iodide on potassium-cresol. Cresol is heated with pulverised potassium hydrate till the latter is dissolved, and the solution is introduced, together with excess of methyl-iodide and a small quantity of methyl alcohol, into a flask connected with an inverted condenser, the violent action which first sets in being moderated by immersing the flask in cold water, and the subsequent action being assisted by a gentle heat. The product washed with water and potash-ley, then dried and rectified, yields methyl-cresol as a colourless liquid lighter than water, having an aromatic odour like that of anise-oil, and boiling without decomposition at 174°. By oxidation with chromic acid mixture it is converted into methyl-paraoxybenzoic or anisic acid (Körner, *Bull. Acad. Belg.* [2] xxiv. 154; *Jahresb.* 1867, p. 326).

Ethyl-paracresol, $C^7H^7O.C^2H^5$, produced by heating paracresol with potassium hydrate, ethyl iodide, and alcohol, is an aromatic liquid insoluble in water and boiling at 186°–188° (Engelhardt a. Latschinoff).

Benzoyl-paracresol, $C^7H^7O.C^7H^5O$, prepared by treating paracresol with benzoyl chloride, is insoluble in water, soluble in a mixture of alcohol and ether, and crystallises by slow evaporation in large six-sided tables melting at 70°. Heated with potash-ley, it is resolved into benzoic acid and paracresol (Engelhardt a. Latschinoff).

Paracresol-sulphuric acid, $C^7H^8SO^4 = C^7H^6(SO^3H)(OH)$, exhibits exactly the same properties whether prepared by the action of sulphuric acid on paracresol, or by treating paratoluidine-sulphuric acid with nitrous acid, whereby it is converted into diazotoluene-sulphuric acid, and decomposing this compound with boiling water. Its *potassium salt* $C^7H^7SO^4K + 2H^2O = C^7H^6(SO^3K)OH + 2H^2O$ crystallises from boiling water in large flat six-sided prisms; from boiling alcohol in needles. The *normal barium salt* $(C^7H^7SO^4)^2Ba$ or $C^{14}H^{12}(S^2O^6Ba)O^2H^2$ is much less soluble in boiling water than the potassium salt, and crystallises on cooling from the saturated solution in a mass of laminæ, which, however, on leaving the crystallising vessel in a warm place, are converted into large plates of the anhydrous salt. A *basic barium salt* $C^{14}H^{12}(S^2O^6Ba)O^2Ba + 4H^2O$ or $C^7H^6SO^4Ba + 2H^2O$ separates on adding baryta-water to a solution of the preceding salt, or to a solution of the potassium salt mixed with barium chloride, as a white precipitate consisting of slender needles. It is but very slightly soluble in water, even at the boiling heat, and crystallises on cooling from the boiling solution in needles. The *normal lead salt* forms very soluble nodules. The paracresolsulphates form with basic lead acetate a basic paracresolsulphate of lead. With ferric chloride they form a solution of a fine violet colour.

Paracresoldisulphates.—The *potassium salt* $C^7H^5(SO^3K)^2OH + 3H^2O$ is obtained by heating potassium paracresolsulphate on the water-bath with Nordhausen sulphuric acid holding sulphuric anhydride in solution; dissolving the product in water; saturating with barium carbonate; and decomposing the filtered solution with potassium sulphate. It is very soluble in water and forms large transparent efflorescent crystals. The *barium salt* $C^7H^5(S^2O^6Ba)''OH + 2\frac{1}{2}H^2O$ separates in long needles on mixing the solution of the potassium salt with barium chloride (Engelhardt a. Latschinoff).

Graebe a. Borgmann (*Zeitschr. f. Chem.* [2] iv. 118) by treating paracresol with potassium chlorate have obtained two chlorinated homologues of quinone:

$$\underset{\text{Dichlorotoluquinone.}}{C^6H(CH^3)Cl^2O^2} \quad \text{and} \quad \underset{\text{Trichlorotoluquinone.}}{C^6(CH^3)Cl^3O^2}$$

ORTHOCRESOL.—This modification has not been obtained quite free from paracresol. It is prepared by fusing the more soluble β-toluene-sulphate of potassium (p. 286) with potassium hydrate, or by decomposing orthotoluidine (liquid toluidine, β-toluidine, Rosenstiehl's pseudotoluidine) with nitrous acid. It is a transparent colourless or yellowish liquid which does not solidify in a freezing mixture, and boils at about 189° (Engelhardt a. Latschinoff).

Methyl-orthocresol is obtained by treating a cooled mixture of methyl-monobromophenol, methyl-iodide, and anhydrous ether with excess of sodium:

$$C^6H^4BrOCH^3 + CH^3I + Na^2 \equiv NaI + NaBr + C^6H^4(OCH^3).CH^3.$$

It is a liquid boiling at 175°, and smelling like rotten apples. By oxidation with chromic acid mixture it is converted into methyl-oxybenzoic acid. Hydriodic acid converts it into a cresol probably identical with the orthocresol above mentioned; but its properties have not been examined (Körner, *Zeitschr. f. Chem.* [2] iv. 327). *Benzoyl-orthocresol* is a thick yellow oil insoluble in water, easily soluble in ether (Engelhardt a. Latschinoff).

Orthocresol-sulphuric acid was obtained by the action of sulphuric acid on orthocresol (containing paracresol). The acid solution was saturated with barium carbonate, and the filtered boiling solution was mixed with baryta-water, which threw down the sparingly soluble barium salt of paracresol-sulphuric acid. The filtrate from the latter yielded, after evaporation and cooling, small nodules consisting of the *basic barium salt* of the ortho-acid $C^{14}H^{12}(S^2O^6Ba)O^2Ba + 4H^2O$. The *normal barium salt* $C^{14}H^{12}(S^2O^6Ba)O^2H^2 + xH^2O$ is uncrystallisable, very soluble in water, soluble in boiling alcohol, from which it separates as a white powder on cooling. The *potassium salt* is easily soluble in water and uncrystallisable (Engelhardt a. Latschinoff).

METACRESOL (*γ-cresol*) is produced by decomposition of thymol (propyl- or isopropyl-phenol). When 100 grms. of thymol are heated in a flask with 35 grms. phosphoric anhydride, propylene gas is given off, and metacresol-phosphoric acid remains in the form of a yellowish liquid; and by fusing this product with potash, dissolving in water, agitating with ether, decomposing the ethereal solution with hydrochloric acid, again dissolving in ether, evaporating, and distilling in a stream of carbon dioxide, metacresol is obtained, together with an oil which has not been further examined. Metacresol is a transparent liquid, which does not solidify in a freezing mixture, boils at 195°–200°, and has a phenolic odour, but without the peculiar character of that of paracresol. *Ethyl-metacresol* is an aromatic oil boiling at 188°–191°. *Benzoyl-metacresol* is a white crystalline mass melting at 38°, and distilling between 290° and 300°.

Metacresolsulphates.—The *potassium salt* $C^7H^6(SO^3K)OH + 2\frac{1}{2}H^2O$ is very soluble in water, and crystallises in needles or short prisms, soluble also in alcohol. The normal *barium salt* $C^{14}H^{12}(S^2O^6Ba)O^2H^2 + 2H^2O$ is easily soluble in water and crystallises in hard nodules. The *basic barium salt* $C^{14}H^{12}(S^2O^6Ba)O^2Ba + 4H^2O$ forms spherical groups of needles very slightly soluble in cold water. The salts of metacresol-sulphuric acid form with basic lead acetate a white precipitate of basic lead metacresolsulphate. Solution of ferric chloride colours them violet (Engelhardt a. Latschinoff).

L. Henry (*Zeitschr. f. Chem.* [2] v. 371), by treating salicylol, $C^6H^4(OH).CHO$, with phosphorus pentachloride in the cold, has obtained the compound $C^6H^4(OH).CHCl^2$, which he designates as dichlorocresol (if really a cresol derivative, it must from its origin be dichloro-metacresol). It crystallises in prisms melting at

82°, is coloured dark red in alcoholic solution by ferric chloride, and when heated with phosphorus pentachloride is converted into *chlorobenzylene dichloride*, $C^6H^4Cl.CHCl^2$.

Dinitrocresols. $C^7H^6(NO^2)^2O$.—A body having this composition is formed, together with other products, by the action of nitrous acid on nitrate of para-amidotoluic acid (see Toluic Acid): it forms yellow crystals melting at 85° (Beilstein a. Kreusler, *Jahresb.* 1866, p. 360). The same compound (melting at 84°) is produced by the action of nitrous acid on ordinary toluidine. Its silver salt $C^7H^5(NO^2)^2OAg$ crystallises in dark orange-coloured slender needles having an iridescent aspect. The red powder known in commerce as *Victoria-yellow* or *Aniline-orange* is a nearly pure salt of dinitrocresol; but the dinitrocresol separated from it is isomeric, not identical, with that just mentioned, as it forms scarcely yellowish crystals melting at 109°–110°, and its silver salt crystallises in thicker needles of a lighter orange-yellow colour. This dinitrocresol dissolves easily in alcohol, ether, and chloroform, producing deep yellow solutions (Martius a. Wichelhaus, *Zeitschr. f. Chem.* [2] v. 440).

CRESOTIC ACID. $C^8H^8O^3 = C^6H^3OH\left\{\begin{matrix}CH^3\\COOH\end{matrix}\right.$.—Kolbe and Lautemann obtained the sodium salt of this acid, together with that of its isomeride, carbocresylic acid, by passing carbon dioxide into cresol holding sodium in solution (ii. 106). The acid thus prepared was paracresotic acid. It melts at 153° (Kolbe a. Lautemann at 147°–150°) (Engelhardt a. Latschinoff), and is coloured violet by ferric chloride.

The same acid has lately been obtained by G. Vogt (*Zeitschr. f. Chem.* [2] v. 577) from xylene as follows: Chloroxylene, $C^6H^3Cl\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right.$, is heated with fuming sulphuric acid, whereby it is converted into the chlorinated sulpho-acid $C^6H^3Cl\left\{\begin{matrix}CH^3\\CH^2SO^3H\end{matrix}\right.$; by fusing the potassium salt of this acid with excess of potassium hydrate, the chlorine and the residue SO^3H are replaced by OH, forming the compound $C^6H^3OH\left\{\begin{matrix}CH^3\\CH^2OH\end{matrix}\right.$, which, by the oxidising action of the potash, is immediatedly converted, with evolution of hydrogen, into the potassium-salt of cresotic acid:

$$C^6H^3OH\left\{\begin{matrix}CH^3\\CH^2OH\end{matrix}\right. + KHO = C^6H^3OH\left\{\begin{matrix}CH^3\\CO^2K\end{matrix}\right. + 2H^2.$$

The cresotic acid separated from this salt by hydrochloric acid crystallises in long prisms melting at 148°.

Orthocresotic acid is produced (together with the preceding) by similar treatment of orthocresol containing paracresol; it is formed much more easily than paracresotic acid. When the mixture of the two acids separated from their sodium salts by hydrochloric acid is fractionally boiled with small portions of water, the last fractions yield paracresotic acid melting at 147°–150°, while the first portions deposit orthocresotic acid in long needles melting at 114°, and likewise coloured violet by ferric chloride. The barium salt of this acid is very soluble in water and in alcohol. *Metacresotic acid*, obtained in like manner from metacresol, is soluble in boiling water and crystallises in needles, melting at 168°–173°, and coloured violet by ferric chloride. Its barium salt is very soluble in water and crystallises in stellate groups of needles (Engelhardt a. Latschinoff).

CRITHMUM. The seeds of samphire (*Cr. maritimum*), an umbelliferous plant growing on rocks on the sea-coast, yield by distillation with water a volatile oil boiling at 175°–178°, and having a sp. gr. of 0·980 at 13°. It oxidises in the air, and is converted by dilute nitric acid into crithmic acid, an acid resembling benzoic acid. The seeds also contain a less volatile oil and a drying fatty oil (Hérouard, *J. Pharm.* [4] iii. 324).

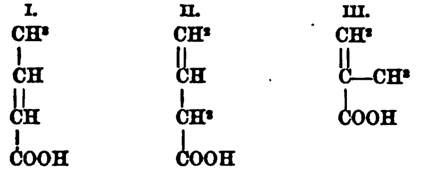
CROCIN. This term, originally applied to the yellow colouring matter of the pods of *Gardenia grandiflora* (ii. 108), has lately also been given to a red substance obtained by decomposition of the natural colouring matter of saffron. (See Saffron, in this volume.)

CROOKESITE. A native selenide of copper, silver, and thallium, from the copper-mine of Skrikerum in Norway, exhibiting the following composition:

Cu	Ag	Fe	Tl	Se		
46·11	1·44	0·63	18·55	—		
46·55	5·04	0·36	16·27	30·86	=	99·08
44·21	5·09	1·28	16·89	32·10	=	99·57

It forms lead-grey compact masses having the hardness of copper-glance, and a sp. gr. of 6·9 (A. E. Nordenskjöld, *Ann. Ch. Pharm.* cxlv. 127).

CROTONIC ACIDS. $C^4H^6O^2$.—This formula represents three isomeric acids, viz.,

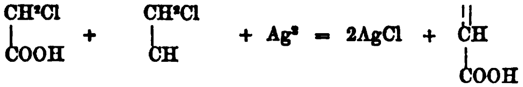


$$\begin{array}{ccc} \text{I.} & \text{II.} & \text{III.} \\ \begin{array}{l} CH^3 \\ | \\ CH \\ \| \\ CH \\ | \\ COOH \end{array} & \begin{array}{l} CH^2 \\ \| \\ CH \\ | \\ CH^2 \\ | \\ COOH \end{array} & \begin{array}{l} CH^2 \\ \| \\ C—CH^3 \\ | \\ COOH \\ \\ \\ \end{array} \end{array}$$

Crotonic. α-crotonic. Methacrylic.

The first of these is the liquid acid, originally called crotonic acid, described by Schlippe as a product of the saponification of croton oil (ii. 112). According to Geuther, however, the saponification of this oil does not yield any acid having the composition $C^4H^6O^2$, the liquid volatile acids obtained by that process being acetic, butyric, and valerianic, with a small quantity of a higher homologue, probably œnanthylic acid, and some of the higher members of the oleic series.

Liquid crotonic acid is obtained by the following processes: 1. By the action of chlorethylidene and metallic silver on monochloracetic acid (Stacewicz, *Zeitschr. f. Chem.* [2] v. 321):



$$\begin{array}{l} CH^2Cl \\ | \\ COOH \end{array} + \begin{array}{l} CH^2Cl \\ | \\ CH \end{array} + Ag^2 = 2AgCl + \begin{array}{l} C^2H^4 \\ \| \\ CH \\ | \\ COOH \end{array}$$

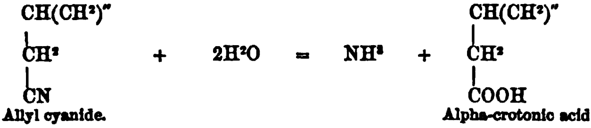
2. By the action of nascent hydrogen on the modification of monochlorocrotonic acid which melts at 59·5° (Fröhlich, p. 511).

Crotonic acid prepared by either of these processes is an oily liquid which does not solidify at −15°; it has an aromatic somewhat pungent odour and blisters the skin. The acid prepared from chlorocrotonic acid boils at 171·9° (Geuther, *Zeitschr. f. Chem.* [2] v. 270); the boiling point of the acid obtained by the second process is said to be 127° (perhaps a misprint for 172°).

Alpha-crotonic Acid (Will a. Körner, *Ann. Ch. Pharm.* cxxv. 257; *Jahresb.* 1863, p. 500; Bulk, *Ann. Ch. Pharm.* cxxxix. 62; *Jahresb.* 1866, p. 315; Claus, *Ann. Ch. Pharm.* cxxxi. 52; *Jahresb.* 1864, p. 336).—This acid is produced: 1. By heating allyl cyanide with caustic potash:

$$C^3H^5.CN + 2H^2O = NH^3 + C^4H^6O^2.$$

Now as allyl alcohol is converted by oxidation into acrylic acid, $CH(CH^2)''.COOH$, its constitution is probably $CH(CH^2)''.CH^2OH$; consequently that of allyl cyanide will be $CH(CH^2)''.CH^2CN$, and that of the acid formed by treating it with alkalis $CH(CH^2)''.CH^2CO^2H$:



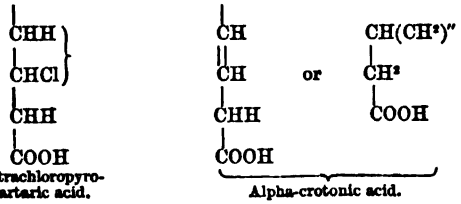
$$\begin{array}{l} CH(CH^2)'' \\ | \\ CH^2 \\ | \\ CN \end{array} + 2H^2O = NH^3 + \begin{array}{l} CH(CH^2)'' \\ | \\ CH^2 \\ | \\ COOH \end{array}$$

Allyl cyanide. Alpha-crotonic acid.

2. By heating citramonochloropyrotartaric acid with an alkali (Swarts, *Jahresb.* 1866, p. 406):

$$C^5H^7ClO^2 = HCl + CO^2 + C^4H^6O^2.$$

The acid thus produced (which has not been particularly described) is commonly said to be crotonic acid; but it is more probably alpha-crotonic acid, as shown by the following formulæ, in the first of which the atoms of chlorine and hydrogen eliminated as hydrochloric acid are connected by a bracket:



$$\begin{array}{l} COOH \\ | \\ \left.\begin{array}{l} CHH \\ | \\ CHCl \end{array}\right\} \\ | \\ CHH \\ | \\ COOH \end{array} \qquad \underbrace{\begin{array}{l} H \\ | \\ CH \\ \| \\ CH \\ | \\ CHH \\ | \\ COOH \end{array} \quad \text{or} \quad \begin{array}{l} CH(CH^2)'' \\ | \\ CH^2 \\ | \\ COOH \end{array}}$$

Citrachloropyrotartaric acid. Alpha-crotonic acid.

3. By the dry distillation of *β*-oxybutyric acid: $C^4H^8O^3 - H^2O = C^4H^6O^2$ (Wislicenus, *Zeitschr. f. Chem.* [2] v. 325).

4. By oxidation of crotonic aldehyde, C^4H^6O (Kekulé, *ibid.* 572). Now this aldehyde, formed by dehydration of acetic aldehyde, [$2C^2H^4O - H^2O = C^4H^6O$], appears to have the constitution $CH^2{=}CH{-}CH^2{-}COOH$ (p. 512); the acid formed from it is therefore constituted according to the formula $CH^2{=}CH{-}CH^2{-}COOH$.

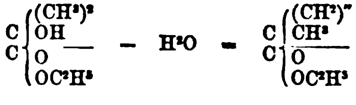
5. By the action of sodium-amalgam on the less volatile of the two chlorocrotonic acids to be presently described (Geuther a. Fröhlich, p. 511).

Alpha-crotonic acid crystallises by cooling from concentrated solutions in needles; by slow evaporation over oil of vitriol, in well-defined monoclinic combinations oP . −P∞ . +P∞ . −P . +*m*P, tabular by predominance of the basal end-face; cleaving distinctly parallel to oP and +*m*P (Knop). It melts at 72°-73°, solidifies at 70·5°, and boils at 183·8° (corr. 187°) without sensible decomposition; volatilises even at ordinary temperatures, diffusing a peculiar odour, distantly resembling that of butyric acid; dissolves in 12 pts. water at 15°. Its salts, with the exception of the silver salt, are easily soluble in water. The *sodium salt* $C^4H^5O^2Na$ crystallises in deliquescent tables; the *potassium salt* is also deliquescent and crystalline. The *barium salt* forms radiate groups of crystals; the *lead salt* $(C^4H^5O^2)^2Pb$, stellate groups of needles, which separate from the evaporated solution after the deposition of prismatic laminæ of a basic salt. The *silver salt* $C^4H^5O^2Ag$ is a white curdy precipitate quickly blackened by light; from a hot-saturated solution this salt separates in dendritic crystals which are decomposed at the boiling heat, with separation of metallic silver.

Nascent hydrogen evolved either by zinc and sulphuric acid, or by water and sodium-amalgam, converts alpha-crotonic acid into an optically inactive acid, $C^4H^8O^2$, identical with ordinary butyric acid (Bulk); according to Körner, however (*Jahresb.* 1866, p. 318), alpha-crotonic acid is not converted into butyric acid by the action of sodium-amalgam.

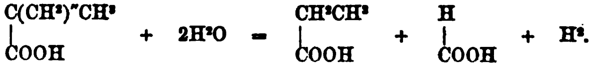
Aqueous alpha-crotonic acid mixed with *bromine* forms a colourless solution, which when evaporated leaves a mixture of a syrupy liquid with a solid acid, which gives out hydrobromic acid; by the action of bromine vapour on crystallised alpha-crotonic acid, only the solid brominated acid is produced. The latter forms monoclinic crystals melting at 78°, solidifying at 75·5°, and moderately soluble in water. It contains 65·72 p. c. bromine, agreeing with the formula of dibromocrotonic acid, $C^4H^4Br^2O^2$, rather than with that of dibromobutyric acid, $C^4H^6Br^2O^2$. The syrupy acid contains a smaller proportion of bromine, and perhaps consists mainly of monobromocrotonic acid, $C^4H^5BrO^2$ (Bulk). According to Körner, on the other hand, bromine forms with alpha-crotonic acid a crystalline acid, agreeing with the formula $C^4H^6Br^2O^2$, melting at 90°, more soluble in water than crotonic acid, and yielding, when treated with alkalis, either monobromocrotonic acid, or by further decomposition, carbon dioxide and a brominated oil having the composition C^3H^5Br.

METHACRYLIC ACID (Frankland a. Duppa, *Chem. Soc. J.* [2] iii. 133).—The ethylic ether of this acid is produced by treating ethyl dimethoxalate with phosphorus trichloride (p. 42):



$$\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}(CH^3)^2\\ \underline{OH\quad}\\ O\\ OC^2H^5\end{array}\right. - H^2O = \begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}(CH^2)''\\ \underline{CH^3\quad}\\ O\\ OC^2H^5\end{array}\right.$$

This ether, which has a very powerful odour of decayed fungi, is resolved by heating with alcoholic potash into alcohol and methacrylic acid, $C(CH)^3(CH^2)''.COOH$, which by distilling its potassium salt with sulphuric acid, is obtained as a colourless oil, smelling slightly like pyrogallic acid, and not solidifying at 0°. It has a strong acid reaction, and its salts exhibit the same tendency as those of the other members of the acrylic series to give off their acid when their solutions are evaporated. The *silver salt* $C^4H^5O^2Ag$ is a white precipitate not much affected by light; the *barium salt* is gummy and very soluble in water; the cupric salt is also moderately soluble. The acid heated with potassium hydrate to the temperature of boiling oil is resolved into propionic and formic acids:



$$\begin{array}{l}C(CH^2)''CH^3\\ |\\ COOH\end{array} + 2H^2O = \begin{array}{l}CH^2CH^3\\ |\\ COOH\end{array} + \begin{array}{l}H\\ |\\ COOH\end{array} + H^2.$$

Methacrylic. Propionic. Formic.

Nomenclature of the Acids $C^4H^6O^2$.—As the saponification of croton-oil does not yield any acid of this composition, Geuther proposes to discard altogether the name 'crotonic acid,' and to designate the liquid acid commonly called by this name (p. 508) as *quartenylic acid*, the corresponding chlorinated acid $C^4H^5ClO^2$ melting at 59·5° and boiling at 194·8°, being called *monochloroquartenylic acid*. The solid acid $C^4H^6O^2$, hitherto called α-crotonic acid, Geuther designates as *tetracrylic acid*, and the chlorinated acid $C^4H^5ClO^2$ melting at 94° and boiling at 206°–211° (p. 511), from which it is formed by the action of sodium-amalgam, as *monochlorotetracrylic acid*.

Bromocrotonic Acids (Kekulé, *Ann. Ch. Pharm. Suppl.* ii. 85; *Jahresb.* 1862, p. 341. Cahours, *Ann. Ch. Phys.* [3] lxvii. 129; *Jahresb.* 1862, p. 316. Bulk, *Ann. Ch. Pharm.* cxxxix. 62; *Jahresb.* 1866, p. 315. Körner, *Ann. Ch. Pharm.* cxxxvii. 233; *Jahresb.* 1866, p. 317).

Monobromocrotonic acid, $C^4H^5BrO^2$, is produced: 1. By treating α-crotonic acid successively with bromine and with an alkali. The crotonic acid then takes up 2 at. bromine, forming an acid isomeric with dibromobutyric acid, $C^4H^6Br^2O^2$; and this, under the influence of the alkali, gives up HBr, and is converted into bromocrotonic acid (Körner).—2. By the action of alkalis on citradibromopyrotartaric acid, the reaction taking place by two stages, carbon dioxide being first removed, and then hydrobromic acid (Kekulé; Cahours). The mode of transformation is exactly similar to that by which crotonic acid is formed from citramonobromopyrotartaric acid, and shows that the bromocrotonic acid thus formed has the structure of a derivative of α-crotonic acid. The mode of preparation adopted by Kekulé is as follows: Calcium citradibromopyrotartrate is prepared by saturating the acid with ammonia, then adding a concentrated solution of calcium chloride, and precipitating with alcohol. The calcium salt, which when once precipitated is but slightly soluble in water, is collected, suspended in water, and the water is boiled. Carbon dioxide is then evolved, and the solution on cooling yields colourless nodules of calcium bromocrotonate. The concentrated solution of this salt mixed with hydrochloric acid yields crystals of bromocrotonic acid, the remainder of which may be extracted from the solution by agitating with ether and evaporating.

Bromocrotonic acid crystallises in long flat needles like benzoic acid. It melts at 65° (Kekulé); 60° (Cahours); and boils, with very slight decomposition, at 228°–230°. It is sparingly soluble in cold, moderately soluble in boiling water; heated with a quantity of water not sufficient to dissolve it completely, it melts below 50°. The aqueous solution saturated at the boiling heat deposits the acid at about 50° in the form of an oil which slowly crystallises. It has a peculiar odour, resembling that of butyric acid.

By *sodium-amalgam* and *water*, bromocrotonic acid is converted into butyric acid, $C^4H^5BrO^2 + 2H^2 = HBr + C^4H^8O^2$. Heated with *bromine* to 100° in sealed tubes, it takes up Br^2, and forms an acid isomeric with tribromobutyric acid, which crystallises in very hard colourless prisms.

The metallic bromocrotonates are all soluble in water, especially in hot water. The *calcium salt* $(C^4H^4BrO^2)^2Ca$ crystallises in nodular groups of small needles. The *silver salt* $C^4H^4BrO^2Ag$ also crystallises in needles.

Ethyl Bromocrotonate, $C^4H^4BrO^2.C^2H^5$, prepared by passing a rapid current of hydrochloric acid gas into a concentrated alcoholic solution of the acid heated nearly to boiling, then separated by water and purified in the usual way, is a colourless aromatic liquid boiling at 192°–193° (Cahours).

Dibromocrotonic acid, $C^4H^4Br^2O^2$ (Cahours, *loc. cit.*).—When the acid $C^4H^5Br^3O^2$, produced by the action of bromine on monobromocrotonic acid, is dissolved in an alkali and heated, it gives up a molecule of hydrogen bromide, and is converted into dibromocrotonic acid. The liquid saturated with hydrochloric acid and left to cool deposits the dibromocrotonic acid as a crystalline precipitate, which may be purified by washing with water and solution in alcohol. By evaporating the alcoholic solution the acid is obtained in long silky needles resembling caffeine. It dissolves readily in ether, and separates in fine crystals by spontaneous evaporation, melts at a gentle heat, and distils at a higher temperature without perceptible alteration.

The metallic dibromocrotonates are mostly crystallisable, and less soluble in boiling water than the monobromocrotonates. The *ethylic ether* is obtained by the action of hydrochloric acid gas on a nearly boiling alcoholic solution of the acid.

Tribromocrotonic acid, $C^4H^3Br^3O^2$.—When dibromocrotonic acid is heated to 120°–125° in sealed tubes with 2 at. bromine, an acid, $C^4H^4Br^4O^2$, isomeric with tetrabromobutyric acid, is formed, which when boiled with alkalis gives up HBr, and is converted into tribromocrotonic acid. This acid, separated from the alkaline solution by hydrochloric acid, dissolves very easily in alcohol and ether, sparingly in cold water, more freely in boiling water, and separates on cooling in slender silky needles very much like those of the dibrominated acid (Cahours).

Chlorocrotonic Acid. $C^4H^5ClO^2$ (O. Fröhlich, *Zeitschr. f. Chem.* [2] v. 270).—When ethyl-diacetic acid, $C^6H^{10}O^3$ (Wanklyn's hydrogen-triacetyl, p. 16), is treated with phosphorus pentachloride, and the product is poured into water, two crystallisable chlorinated acids are obtained having the composition $C^4H^5ClO^2$, together with an oil which appears to consist of the corresponding ethylic ethers. One of those acids melts at 94°, and boils at 206°–211°, is very soluble in water, distils slowly with aqueous vapour, and is converted by treating its sodium salt with sodium-amalgam into α-crotonic acid. The other acid (to which the following description applies) melts at 59·5°, is but slightly soluble in water, and passes over very easily with aqueous vapour, and is converted by sodium-amalgam into liquid crotonic acid.

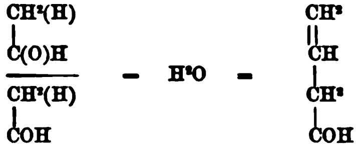
Chlorocrotonic acid, purified by repeated distillation from adhering colouring matter, forms white, very light needle-shaped crystals; from a concentrated aqueous solution it separates in colourless transparent four-sided prisms with oblique end-faces. It melts at 59·5° to a colourless liquid, which solidifies again in the crystalline form at 55·5°. Heated above its melting point it partly sublimes, and begins to boil at 194·8° (corr.); the liquid distillate solidifies very quickly to a white dense crystalline mass. It has a faint somewhat pungent odour and acid taste. When kept in close vessels it sublimes even at ordinary temperatures; 1 pt. of it dissolves in 79 pts. water at 7°; in alcohol and ether it dissolves very easily. It is a rather strong acid, quickly decomposing carbonates.

Potassium Chlorocrotonate, $C^4H^4ClO^2K + H^2O$, prepared by neutralising the acid with potassium carbonate and gradual evaporation over sulphuric acid, forms small colourless plates and needles apparently belonging to the rhombic system; they are very soluble, become moist in the air, but effloresce over oil of vitriol. The *sodium salt* $2C^4H^4ClO^2Na + H^2O$, prepared in like manner, forms satiny crystals, often in feathery groups, also very soluble in water and in alcohol, and efflorescing over sulphuric acid. An *acid ammonium salt*, $C^4H^4ClO^2(NH^4).C^4H^5ClO^2 + H^2O$, gradually separates in crystalline crusts from a solution of the acid in excess of ammonia left over sulphuric acid. The *thallium salt*, prepared by heating the acid with thallium carbonate and water, separates on cooling as a crystalline powder, and the solution on further evaporation deposits elongated monoclinic tables containing $C^4H^4ClO^2Tl + H^2O$. The *silver salt* $C^4H^4ClO^2Ag$ is a white crystalline precipitate, nearly insoluble in cold water, and separating from a hot-saturated aqueous solution in feathery groups of laminæ having a satiny lustre and quickly blackening when exposed to light.

The *barium salt* $(C^4H^4ClO^2)^2Ba.H^2O$, obtained by neutralisation, crystallises in shining, mostly four-sided prisms with oblique end-faces, sometimes flattened into tables; it is easily soluble in water. The *calcium salt* $(C^4H^4ClO^2)^2Ca + 3H^2O$ forms hollow prisms, very soluble in water, efflorescing over sulphuric acid. The *magnesium salt* $(C^4H^4ClO^2)^2Mg + 5H^2O$ forms thin transparent monoclinic tables, efflorescent and very soluble in water. The *manganese salt* $(C^4H^4ClO^2)^2Mn + 2H^2O$ forms very soluble colourless rhombic crystals, mostly thick tables, which slowly effloresce over sulphuric acid. The *cobalt salt* $(C^4H^4ClO^2)^2Co + 6H^2O$ forms very soluble rhombic tables having a peach-blossom colour and strong lustre, and quickly efflorescing over sulphuric acid. The *nickel salt* $(C^4H^4ClO^2)^2Ni + 6H^2O$ forms light green crystals of similar form and properties. The *zinc-salt* $2(C^4H^4ClO^2)^4Zn + 5H^2O$ forms colourless shining rhombic tables, very soluble, and not efflorescing even over sulphuric acid. The *cupric salt* $(C^4H^4ClO^2)^2Cu$, produced by boiling the crystallised acid with water and cupric carbonate, separates from the hot-filtered solution by slow evaporation in blue rhombic prisms, or in dark-green quadratic combinations of prism and pyramid, the former crystallising out at comparatively low, the latter at higher temperatures. The green crystals contain $2(C^4H^4ClO^2)^2Cu + 3H^2O$; the blue crystals appear to contain more water, and turn green in the air-bath at 80°. The *lead salt* $(C^4H^4ClO^2)^2Pb + 4H^2O$ forms concentric groups of silky needles, rather sparingly soluble in water, and efflorescing gradually over sulphuric acid.

Ethyl Chlorocrotonate, $C^4H^4ClO^2.C^2H^5$, is prepared by digesting the crystallised acid with twice its volume of absolute alcohol saturated with hydrochloric acid in a well-closed vessel at a gentle heat, for several days and with frequent agitation. When purified in the usual way, it is a colourless oily liquid, having a pleasant aromatic odour and cooling taste. Boils at 161·4° (corr.), and has a sp. gr. of 1·113 at 15°. Dissolves slightly in water, easily in alcohol and ether. Decomposed by heating with sodium carbonate. The *methylic ether* $C^4H^4ClO^2.CH^3$, prepared in like manner, is a colourless oily liquid, having a pungent ethereal odour and strongly cooling taste. Boils at 142·4° (corr.). Sp. gr. 1·143 at 15°. Less soluble in alcohol than the ethylic ether; nearly insoluble in water.

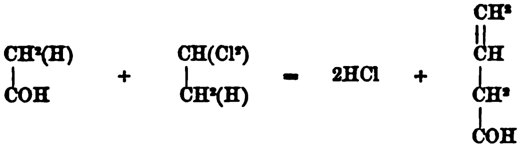
CROTONIC ALDEHYDE. $C^4H^6O = CH^2{=}CH—CH^2—COH$. *Tetracrylic aldehyde* (Kekulé, *Zeitschr. f. Chem.* [2] v. 572; Paterno a. Amato, *ibid.* 637; Lwow, *ibid.* vi. 245).—Produced: 1. By heating acetic aldehyde with zinc chloride and a little water to 100°, the reaction consisting in the elimination of 1 mol. water from 2 mol. acetic aldehyde (Kekulé), as shown by the following equation, in which the eliminated atoms are enclosed in brackets:



$$\frac{\begin{array}{l} CH^2(H) \\ | \\ C(O)H \end{array}}{\begin{array}{l} CH^2(H) \\ | \\ COH \end{array}} - H^2O = \begin{array}{l} CH^2 \\ \| \\ CH \\ | \\ CH^2 \\ | \\ COH \end{array}$$

Acetic aldehyde (2 mol.). Crotonic aldehyde.

2. By heating acetic aldehyde with ethylidene chloride in sealed tubes (Paterno a. Amato):



$$\begin{array}{l} CH^2(H) \\ | \\ COH \end{array} + \begin{array}{l} CH(Cl^2) \\ | \\ CH^2(H) \end{array} = 2HCl + \begin{array}{l} CH^2 \\ \| \\ CH \\ | \\ CH^2 \\ | \\ COH \end{array}$$

Crotonic aldehyde is a colourless liquid, having an extremely pungent odour, and boiling at 103°–105° (Kekulé). In contact with the air it oxidises to α-crotonic acid (p. 509). By phosphorus pentachloride it is converted into a liquid chloride, $C^4H^6Cl^2$, having an ethereal odour, a sp. gr. of 1·138, and boiling at 125°. This chloride treated with alcoholic potash is converted into C^4H^5Cl, a liquid lighter than water, and having the odour of chlorinated hydrocarbons in general.

Crotonic aldehyde saturated with hydrochloric acid gas is converted by direct addition into chlorobutyric aldehyde, C^4H^7ClO, which crystallises in white needles insoluble in water, sparingly soluble in alcohol, melting at 96°–97°, and scarcely volatilising with vapour of water (Kekulé).

Trichlorocrotonic Aldehyde.—A large quantity of aldehyde is now produced in Berlin in the purification of alcohol by passing it over charcoal, the alcohol being oxidised, partly by contact with the air, partly by oxygen condensed in the charcoal. Now when the mixture of aldehyde and alcohol thus produced is treated with chlorine, for the manufacture of chloral—hydrochloric acid being formed at the same time—this hydrochloric acid acts as a dehydrating agent upon the acetic aldehyde, converting it into crotonic aldehyde, in the same manner as the zinc chloride in the process above mentioned; and lastly this crotonic aldehyde, as fast as it is formed, is converted by the free chlorine into trichlorocrotonic aldehyde, $C^4H^3Cl^3O$ (*Communication made by Dr. Hofmann to the Chemical Society*, April 21, 1870).

CRUORIN. See Blood (p. 352).

CRYOPHYLLITE. A variety of mica occurring, together with lepidomelane, danalite, and a zircon-like mineral, in the granite of Rockport, Massachusetts. It forms six-sided prisms belonging to the rhombic system, often two inches long, having perfect basal cleavage and two optic axes inclined at an angle of 55° to 60°. Colour, dark emerald-green in the direction of the principal axis, brownish-red in the direction of the secondary axes. Streak, light-grey to greenish. Lustre on the cleavage-faces, resinous. Hardness = 2 to 2·5. Sp. gr. = 2·909. Analysis gave:

SiO^2	SiF^4	Al^2O^3	Mn^2O^3	Fe^2O^3	FeO	MgO	K^2O	Li^2O	
51·49	3·42	16·77	0·34	1·97	7·98	0·76	13·15	4·06	= 99·94

with traces of soda and rubidia, agreeing with the formula

$$3(M^2;M'')O.R^2O^3.6SiO^2,$$

which is included in the general formula of the orthosilicates M^4SiO^4 or $2M^2O.SiO^2$ (J. P. Cooke, jun., *Sill. Am. J.* [2] xliii. 217).

CRYPTOPHANIC ACID. $C^5H^9NO^5$ or $C^{10}H^{18}N^2O^{10}$ (Thudichum, *Chem. Soc. J.* [2] viii. 132).—An acid existing in normal human urine. To prepare it, the urine is treated with excess of milk of lime; the liquid filtered from the gypsum is acidulated and evaporated to a syrup; and this, after filtration from the salt-cake, is treated with strong alcohol, which separates calcium cryptophanate as a dark flaky mass. The impure calcium salt is dissolved in water and mixed with solution of neutral lead acetate, whereby a dark-coloured precipitate is formed, from which the mother-liquor is to be filtered. The filtrate containing lead cryptophanate is treated with strong alcohol, whereby the lead salt is thrown down in white flakes, from which the acid may be liberated by hydrogen sulphide.

Cryptophanic acid is an amorphous gummy mass, transparent and nearly colourless, soluble in water in all proportions, less soluble in alcohol, which indeed produces a precipitate in the aqueous solution; ether added to the alcoholic mixture produces a fresh precipitate. It has a freely acid taste, decomposes alkaline and earthy carbonates, forming aqueous solutions of the corresponding cryptophanates. Its solution forms with lead acetate a copious thick white precipitate soluble in excess of lead acetate; with mercuric acetate a similar precipitate; with silver nitrate a very slight precipitate. The free acid is not precipitated by mercuric chloride or by cupric acetate. An ammoniacal solution of silver nitrate mixed with ammonium cryptophanate immediately becomes very dark, and on standing almost black (red when diluted), depositing metallic silver as a black powder. Silver nitrate and excess of nitric acid, added to a solution of cryptophanic acid containing urea, produces after some time a specular deposit of metallic silver.

The cryptophanates of the alkali-metals are very soluble in water; the sodium salt is not precipitated from its aqueous solution by alcohol. The cryptophanates of the earth-metals are precipitated by excess of alcohol. Boiled with a great excess of alkaline cupric solution, they reduce the cupric to cuprous oxide, which remains in solution, but is deposited if the solution is concentrated and kept from access of air. The alkaline solution exhibits a blue fluorescence. With mercuric nitrate, the solutions of the earthy cryptophanates give a bulky white precipitate: hence the ordinary estimation of urea in urine by this reagent requires a correction for cryptophanic acid, which may amount to 5 to 10 per cent.

The composition of many of the metallic cryptophanates may be represented by the formula $C^5H^7NO^5M''$, the acid $C^5H^9N^2O^6$ being regarded as bibasic. But there are also cryptophanates containing $C^{10}H^{13}N^2N^9\acute{M}^3$ or $(C^{10}H^{13}N^2O^9)^2\acute{M}^3$, and others containing $C^{10}H^{14}N^2O^9M''$: thus there is a calcium salt containing $(C^{10}H^{13}N^2O^9)^2\tilde{Ca}^3$, and another containing $C^{16}H^{14}N^2O^9Ca''$. On the whole, perhaps the constitution of these salts is best represented by regarding cryptophanic acid as a quadribasic acid, containing in the free state $C^{10}H^{16}N^2O^9.H^2O$; but they require further examination.

CRYPTOPINE. $C^{23}H^{25}NO^5$ (T. and H. Smith, *Pharm. J. Trans.* [2] viii. 595, 716). —A base existing in very small quantity in opium, being found in the alcoholic wash-liquors of crude morphine. To separate it, the alcoholic liquid is nearly neutralised with dilute sulphuric acid; the alcohol is evaporated; and the residue, dissolved in hot water, is precipitated with excess of milk of lime. The precipitate, containing the cryptopine, together with many other substances, is exhausted with hot alcohol; the alcohol is distilled off; and the pitchy substance (chiefly containing thebaine) which separates from the watery residue, is repeatedly boiled with alcohol. The resulting solution, after standing for some days, solidifies to a soft crystalline mass of thebaine. This is pressed, dissolved in the smallest possible quantity of very dilute hydrochloric acid (so that the liquid does not become acid), and repeatedly evaporated to the crystallising point, whereupon hydrochloride of thebaine crystallises out first, and the last mother-liquors, after standing for a considerable time, yield hydrochloride of cryptopine (or a mixture of the hydrochlorides of thebaine and cryptopine). For the complete separation of the two bases, the last crystallisation is once more crystallised from the smallest possible quantity of hot water, and the soft cauliflower-like mass which separates is dried and boiled with 5 pts. of alcohol. The alcoholic solution then yields, first, several hard crystallisations of thebaine hydrochloride, and finally from the last mother-liquor, soft crystalline masses of cryptopine hydrochloride, to be decolorised with animal charcoal. Five tons of opium yielded only 5 oz. of this salt.

Cryptopine separated from the hydrochloride by ammonia crystallises from boiling alcohol in microscopic six-sided prisms or tables. It melts at 175°; solidifies again at 171°; is nearly insoluble in water, ether, turpentine-oil, and benzol, slightly soluble in alcohol (1 pt. in 1265), more soluble in chloroform. It forms neutral and acid salts, which have a bitter taste, with cooling after-taste. The neutral hydrochloride $C^{23}H^{25}NO^5.HCl + 5H^2O$ is distinguished by its inclination to separate under certain circumstances in the gelatinous form. The acid hydrochloride contains $C^{23}H^{25}NO^5.2HCl + 6H^2O$; the platinochloride, $2(C^{23}H^{25}NO^5.HCl)PtCl^4$.

With strong sulphuric acid cryptopine produces a blue colour, changing to orange-yellow on addition of saltpetre; if thebaine is present, the blue has a tinge of violet; the somewhat fainter blue produced in like manner by papaverine is changed to green by addition of saltpetre. From pseudomorphine, which is coloured brown by sulphuric acid and blue by ferric chloride, cryptopine is distinguished by its solubility in potash, and by not being coloured by ferric chloride.

CUMENE. $C^9H^{12} = C^6H^5.C^3H^7$.—See BENZENE, HOMOLOGUES OF (p. 295).

CUMENYL SULPHYDRATE or **CUMIC MERCAPTAN,** $C^9H^{12}S = C^9H^{11}SH$, is formed by the action of zinc and sulphuric acid on cumene-sulphuric chloride (obtained by triturating the sodium-salt of cumene-sulphuric acid with phosphorus pentachloride, and mixing the product with water). It crystallises in inodorous nacreous laminæ melting at 86°–87° (Beilstein a. Kögler, *Jahresb.* 1865, p. 559).

CUMIC or **CUMINIC ACID,** $C^{10}H^{12}O^2 = C^9H^{11}.COOH = C^6H^4(C^3H^7).COOH$ (ii. 178).

Bromocumic acid, $C^{10}H^{11}BrO^2$, is formed, together with cumic acid, by exposing finely pulverised silver cumate to the action of bromine vapour. When the portion of the product which is soluble in ether is treated ten times with boiling water, the cumic acid dissolves, while the much more abundant insoluble portion consists, after recrystallisation from ether, of pure bromocumic acid. This acid is mostly crystalline, melts at 146°, is nearly insoluble in boiling, and quite insoluble in cold water, slightly soluble in cold alcohol, easily soluble in ether. Its silver salt is insoluble in water, and is not decomposed by water even at 150° (Naquet a. Louguinine, *Compt. rend.* lxii. 1031).

CUMIC or **CUMINIC ALDEHYDE.** $C^{10}H^{12}O = C^9H^{11}.CHO = C^6H^4(C^3H^7).CHO$. —Gerhardt found that this compound heated with potassium gives off hydrogen and forms cumyl-potassium, as represented by the equation $2C^{10}H^{12}O + K^2 = 2C^{10}H^{11}KO + H^2$. According to Church (*Phil. Mag.* [4] xxv. 522), the reaction is less simple, and the quantity of hydrogen evolved is smaller than the preceding equation requires. When a mixture of cumic aldehyde and benzene (or other hydrocarbon from coal-naphtha) is heated with sodium-amalgam, the sodium-compounds of cymyl alcohol and cumyl are produced in equivalent quantities, and on treating the product with water, these sodium compounds are decomposed, yielding cymyl alcohol and cumic aldehyde:

$$\underset{\substack{\text{Sodium}\\\text{Cymylate.}}}{C^{10}H^{13}NaO} + H^2O = \underset{\substack{\text{Cymyl}\\\text{alcohol.}}}{C^{10}H^{14}O} + NaHO.$$

$$\underset{\substack{\text{Sodium}\\\text{cumyl.}}}{C^{10}H^{11}NaO} + H^2O = \underset{\substack{\text{Cumic}\\\text{aldehyde.}}}{C^{10}H^{12}O} + NaHO.$$

At the same time there is formed a viscid oily body, boiling above 300°, having the composition of dicumyl, $(C^{10}H^{11}O)^2$. This latter is more easily formed, together with cymyl cumate, by treating the product of the reaction of sodium on cumic aldehyde with cumyl chloride. If benzoyl chloride be used instead of cumyl chloride, the products are cymyl benzoate and cumyl-benzoyl:

$$\underset{\substack{\text{Sodium}\\\text{cymylate.}}}{C^{10}H^{13}NaO} + \underset{\substack{\text{Sodium}\\\text{cumyl.}}}{C^{10}H^{11}NaO} + \underset{\substack{\text{Benzoyl}\\\text{chloride.}}}{2C^7H^5OCl} = \underset{\substack{\text{Cymyl}\\\text{benzoate.}}}{\left.\begin{matrix}C^{10}H^{13}\\C^7H^5O\end{matrix}\right\}O} + \underset{\substack{\text{Cumyl}\\\text{benzoyl.}}}{\left.\begin{matrix}C^{10}H^{11}O\\C^7H^5O\end{matrix}\right\}} + 2NaCl.$$

According to Claus (*Jahresb.* 1866, p. 354), cumic aldehyde treated in ethereal solution with sodium-amalgam, yields, together with sodium cumate, a neutral body, C^9H^8O, which crystallises in needles, and is coloured violet-blue or cherry-red by strong sulphuric acid.

Cumic aldehyde, or Roman cumin-oil, oxidised with *chromic acid* is converted into terephthalic acid (De la Rue a. Müller, *Jahresb.* 1861, p. 425). According to Buliyinsky a. Erlenmeyer (*ibid.* 1866, p. 371), the products are cumic acid and a solid acid intermediate in composition between terephthalic acid, $C^8H^6O^4$, and insolinic acid, $C^9H^8O^4$.

CUMIDINE, $C^9H^{13}N$, or *Amidocumene*, $C^9H^{11}(H^2N) = C^6H^4(NH^2).C^3H^7$.—This base, formed by the action of ammonium sulphide on nitrocumene, is described in the Dictionary, vol. ii. p. 174, under the name of *Cumenylamine*, and regarded as homologous with benzylamine, which latter, at the time when that article was written, was supposed to be identical with toluidine. Subsequent researches have, however, shown that the hydrocarbons homologous with benzene give rise to two series of isomeric bases, the one series, viz. toluidine and its homologues, being formed by reduction of nitrotoluene, &c., and having the amidogen-group NH^2 situated in the principal chain, the other series, viz. benzylamine and its homologues, being formed, like the bases of the ethyl series, by the action of ammonia on the corresponding alcoholic chlorides, and having the amidogen in one of the lateral chains. (See Aromatic Series, p. 203.) Cumidine then is homologous, not with benzylamine, but with toluidine; the true cumenylamine, $C^6H^5.C^3H^6NH^2$, has not yet been discovered.

Cumidine is formed by distilling amidocumic acid (ii. 179) with anhydrous baryta, or solid potassium hydrate (Cahours, *Jahresb.* 1868, p. 324):

$$C^{10}H^{13}NO^2 + BaO = CO^3Ba + C^9H^{13}N.$$

It may be conveniently prepared by reducing nitrocumene with tin and hydrochloric acid. The hot somewhat dilute filtrate yields shining laminæ of *cumidine stannosochloride*, $C^9H^{13}N.HCl.SnCl^2$, from which, by precipitating the tin with hydrogen sulphide, *cumidine hydrochloride*, $C^9H^{13}N.HCl$, is obtained in long prismatic crystals; and this salt decomposed by ammonia, yields cumidine as a white flocculent precipitate, which crystallises from hot water or from alcohol in long silky needles melting at 62° (L. Schaper, *Zeitschr. f. Chem.* [2] iii. 12).

CUMONITRILAMINE, $C^{10}H^{12}N^2$, or *Amidocumonitrile*, $C^{10}H^{10}(NH^2)N$ (Czumpelik, *Zeitschr. f. Chem.* [2] v. 437).—Cumonitrile, $C^{10}H^{11}N$, added by drops to a cooled mixture of strong nitric and sulphuric acids, is converted into crystalline nitrocumonitrile, $C^{10}H^{10}(NO^2)N$; and this compound subjected in alcoholic solution to the action of nascent hydrogen (from zinc and hydrochloric acid) is converted into cumonitrilamine. When the reaction is complete (*i.e.* when a sample mixed with water no longer becomes turbid) the liquid filtered from the zinc is mixed with sufficient caustic soda to redissolve the separated zinc-hydrate; the alcoholic layer which contains the base is decanted; the alcohol distilled off; the remaining liquid mixed with water and agitated with ether to dissolve out the base; and the ethereal solution separated from the watery layer is freed from ether over the water-bath. On distilling the remaining liquid over an open fire, the base passes over at about 305° as an oily aromatic liquid.

Cumonitrilamine is sparingly soluble in water, and crystallises therefrom in large needles; in alcohol and ether on the other hand it dissolves readily, and is not so easily obtained from these solutions in good crystals. It melts at about 45°, and boils at about 305°. With acids it forms well-crystallised salts. The *hydrochloride* crystallises in colourless six-sided tables; the *platinochloride*, $2(C^{10}H^{12}N^2.HCl).PtCl^4$, also crystallises well. The *sulphate* and *nitrate* crystallise in needles.

In the preparation of cumonitrilamine from nitrocumonitrile an intermediate compound is also produced.

CUMOYLIC ACID. Syn. with Hydrocinnamic Acid. See Cinnamic Acid (p. 468).

CUMYLAMINE. $C^{10}H^{15}N$; better called Cymylamine (*q.v.*).

CUMYL-BENZOYL. $C^{10}H^{11}O.C^7H^5O$ (p. 505).

CUMYLENE-DIAMINE, $C^9H^{14}N^2 = (C^9H^{10})''H^4N^2$, produced by distilling dinitrocumene with acetic acid and iron, is a splendidly crystalline base melting at 47° (Hofmann, *Compt. rend.* lv. 781).

CUPREIN. This name is given by Breithaupt to a hexagonal form of cuprous sulphide, Cu^2S, which, according to his observations, occurs in nature more frequently than the rhombic form, copper-glance (ii. 74). It forms hexagonal prisms, ∞P, of 120°, combined with 2P, P, and oP; also twin-crystals. Angle 2P : oP = 117° 53′. Cleavage basal. Fracture uneven to conchoïdal. Sp. gr. = 5·50 to 5·586. Hardness = 3¾. Colour blackish-grey, but lighter than that of copper-glance (*Jahresb.* 1863, p. 794).

CUPROSACETYL-COMPOUNDS. See Acetylene (p. 35).

CURARINE. According to W. Preyer (*Bull. Soc. Chim.* [2] iv. 238), this base has the composition $C^{10}H^{15}N$. It is very hygroscopic; has a very bitter taste; crystallises in colourless four-sided prisms; dissolves freely in water and alcohol, less easily in chloroform and amyl alcohol; and is insoluble in anhydrous ether, benzol, turpentine, and carbon bisulphide. It blues litmus very slightly, acquires a splendid and permanent blue colour in contact with sulphuric acid, purple-red with nitric acid, and violet with potassium dichromate and sulphuric acid (like that of strychnine, but more permanent). Its hydrochloride, nitrate, sulphate, and acetate are crystallisable. Dragendorff (*Zeitschr. f. Chem.* [2] iii. 28) also finds that curarine is quite distinct from strychnine, and that a very active curara occurs in commerce, in which neither strychnine nor brucine can be detected. On the physiological action of curarine and curara, see Cl. Bernard, *Compt. rend.* lx. 1327; Bert, *Chem. Centr.* 1865, p. 229; Schnetzler, *N. Arch. ph. nat.* xxiv. 318; *Jahresb.* 1865, p. 456.

CURCUMIN. The resinous colouring matter of tumeric-root (ii. 186). Respecting the changes of colour which it exhibits with boric acid, see Schlumberger (*Bull. Soc. Chim.* [2] v. 194; *Jahresb.* 1866, p. 652). Boiled in alcoholic solution with boric acid, it forms a compound which separates from the cooled solution, on addition of water, as a cinnabar-red precipitate, and is decomposed by boiling with water, boric acid dissolving and a yellow resin separating. This resin, called *pseudocurcumin*, is distinguished from curcumin by not being reddened by boric acid, and by assuming a greenish-grey colour in contact with alkalis. It separates from its solutions on evaporation in vitreous dark yellow laminæ, insoluble in water, soluble in ether and in benzol, very soluble in alcohol. When the orange-yellow solution of the boric acid compound is boiled with a mineral acid, it turns blood-red, and deposits on cooling a granular nearly black substance called *rosocyanin*, which, when purified by crystallisation from a mixture of hot alcohol and acetic acid, and washing with ether, forms a mass of interlaced needles with beautiful green reflex. The alcoholic solution of rosocyanin has a red colour, and when boiled becomes first blood-red and then yellow, in which state it contains pseudocurcumin. The red alcoholic solution mixed with a drop of soda or ammonia, acquires a pure blue colour, changing on saturation with an acid to the orginal rose-red tint (Schlumberger).

CYAMELIDE, *n*CNHO, is produced, together with cyanic acid, when a mixture of urea and phosphoric anhydride in equivalent proportions is distilled at 40°, in a flask provided with a series of condensing tubes, a considerable quantity of cyanic acid condensing in the first, and cyamelide chiefly in the second (Weltzien, *Ann. Ch. Pharm.* cvii. 219). A solution of cyamelide in strong sulphuric acid deposits the unaltered substance, on dilution with water, as an amorphous precipitate; but if the solution be heated till decomposition begins (attended with evolution of carbon dioxide), water no longer forms a precipitate, but the diluted solution yields after some time crystals of anhydrous cyanuric acid (Weltzien, *ibid.* cxxxii. 222).

CYANACETIC ACID. See Acetic Acid (p. 19).

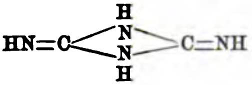
CYANAMIDE. $CH^2N^2 = CN(NH^2)$.—Beilstein a. Geuther (*Ann. Ch. Pharm.* cviii. 88) obtained this compound by heating sodamide in a stream of carbon dioxide:

$$2NH^2Na + CO^2 = CN(NH^2) + 2NaHO.$$

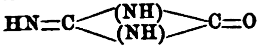
Cyanamide unites directly with *glycocine*, $C^2H^5NO^2$, forming glycocyamine, $C^3H^7N^3O^2$, and with *methyl-glycocine* or *sarcosine*, $C^3H^7NO^2$, producing creatine, $C^4H^9N^3O^2$ (p. 501).

Cyanamide unites with *aldehyde*, with elimination of water, forming the compound $C^9H^{14}N^6O = 3CH^2N^2 + 3C^2H^4O - 2H^2O$. This compound dissolves in alcohol, and is precipitated therefrom by ether, chloroform, benzol, aniline, and carbon bisulphide. It is decomposed by heat, giving off an oily body having the odour of an organic base. A similar compound is formed with *valeral* (Knop, *Ann. Ch. Pharm.* cxxx. 253).

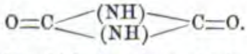
Dicyanodiamide. $C^2H^4N^4 = N^2\left\{\begin{matrix}(CN)^2\\H^4\end{matrix}\right. = (CN)^2(NH^2)^2$ (ii. 189).—Strecker (*Kurzes Lehrbuch d. organischen Chemie*) represents this compound by the structural formula



This formula suggests the possibility of replacing one or both of the imidogen groups NH, which are connected with only one carbon-atom (and may therefore be expected to be more loosely attached than the other two) by oxygen, which would give the compounds



and



The second of these is dicyanic acid, $C^2N^2H^2O^2$, which Poensgen obtained from cyanocarbamide (see Dicyanic Acid); the first is dicyanamic acid, a compound holding an intermediate position between dicyanic acid and dicyanodiamide, just as ammelide and ammeline are intermediate between cyanuric acid and cyanuramide or melamine:

$$\underset{\text{Cyanuric acid.}}{\left.\begin{matrix}C^3N^3\\H^3\end{matrix}\right\}O^3}\qquad\underset{\text{Ammelide.}}{\left.\begin{matrix}C^3N^3\\H^4\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}}\qquad\underset{\text{Ammeline.}}{\left.\begin{matrix}C^3N^3\\H^5\end{matrix}\right\}\begin{matrix}N^2\\O\end{matrix}}\qquad\underset{\text{Melamine.}}{\left.\begin{matrix}C^3N^3\\H^6\end{matrix}\right\}N^3}$$

$$\underset{\text{Dicyanic acid.}}{\left.\begin{matrix}C^2N^2\\H^2\end{matrix}\right\}O^2}\qquad\underset{\text{Dicyanamic acid.}}{\left.\begin{matrix}C^2N^2\\H^3\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}}\qquad\underset{\text{Dicyanodiamide.}}{\left.\begin{matrix}C^2N^2\\H^1\end{matrix}\right\}N^2}$$

Dicyanamic acid is produced by boiling dicyanodiamide with baryta-water as long as ammonia is thereby evolved. On removing the excess of baryta with carbonic acid, a solution of barium dicyanamate is obtained, which, when slightly acidulated with nitric acid and mixed with silver nitrate, yields the *silver salt* $C^2H^2N^3OAg$ as a white curdy precipitate, soluble in ammonia, and crystallising therefrom by slow evaporation in thin colourless laminæ, mostly grouped in tufts. The *copper salt* is obtained by decomposing the silver salt with a moderately warm solution of cupric chloride, and separates on cooling in sky-blue shining crystals containing $(C^2H^2N^3O)^2Cu + 8H^2O$, which give off 6 mol. water at 90°, assuming a dark green colour; at a higher temperature the salt blackens and decomposes. It dissolves sparingly in cold, more easily in warm water; the aqueous solution when heated to boiling deposits a dark green insoluble powder.

By passing hydrogen sulphide through water in which the cupric salt is suspended, and evaporating the filtrate, the *hydrogen salt* or *free acid* $C^2H^3N^3O$ is obtained in groups of small white needles.

Dicyanamic acid contains the elements of cyanamide, CN^2H^2, and cyanic acid, CNHO, and its potassium salt may be produced by heating cyanamide with potassium cyanate in a test-tube, or by leaving cyanamide for twenty-four hours in contact with aqueous solution of potassium cyanate. Part of the cyanamide then dissolves, and on heating the liquid with nitric acid to decompose the remaining cyanic acid, a solution is obtained which yields the salts above described with silver nitrate and cupric chloride (F. Hallwachs, *Zeitschr. f. Chem.* [2] iv. 515).

CYANAMIDOBENZOIC ACID. See Benzoic Acid (p. 318).

CYANIC ACID. CNHO or N≡C—OH or $\left.\begin{matrix}CN\\H\end{matrix}\right\}O$.—The physical properties of this acid have lately been investigated by Troost a. Hautefeuille (*Zeitschr. f. Chem.* [2] v. 149, 188, 497, 629). 1. The vapour-density was found in two determinations to be 1·51 and 1·50, the calculated number being 1·488. To prevent condensation of the cyanic acid vapour to cyamelide, the vapour evolved by heating dry cyanuric acid or pure cyamelide to 440°, was passed into a globe previously exhausted of air and heated to the temperature at which it was to be afterwards sealed.

2. The absolute coefficient of expansion of the liquid acid was found to be = 0·000300 from −20° to −14°; 0·0006999 from −20° to 0°; and = 0·0008450 from −3° to 0°. It increases therefore very rapidly as the temperature rises.

3. The sp. gr. of the liquid acid is 1·1558 at −20°, whence, by means of the expansion coefficient above given, the sp. gr. at 0° is found to be 1·140.

4. The tension of the vapour of cyanic acid evolved from cyanuric acid or cyamelide increases with the temperature, and the transformation ceases as soon as the cyanic acid vapour exerts upon the solid isomeric compound from which it is formed, a pressure which is determinate for each temperature, viz.,

Temp.	Tension	Temp.	Tension	Temp.	Tension
160°	56 mm.	195°	125 mm.	251°	285 mm.
170	68	215	157	330	740
180	94	227	180	350	1,200

5. The transformation of 1 gram of cyanic acid into cyamelide is accompanied by the evolution of 410 units of heat; on the other hand, 1 gram of cyamelide, in passing into cyanuric acid, absorbs 76 units of heat: hence cyanuric acid in changing into cyamelide must give off heat. This allotropic transformation, contrary to what is generally observed, is accompanied by a decrease of density at a temperature near 20°: for the density of cyanuric acid is 2·768 at 0°; 2·500 at 19°; 2·228 at 24°; 1·725 at 48°, whereas that of cyamelide is 1·974 at 0° and 1·774 at 24°.

6. *Heat of Combustion of Cyanic Acid and its Polymerides.*—Cyanuric acid is completely oxidised by a moderately concentrated solution of hypochlorous acid, yielding water, carbon dioxide, and nitrogen; cyanic acid in like manner yields carbon dioxide

and nitrogen chloride, whereas cyamelide is only imperfectly oxidised even by very concentrated hypochlorous acid. Cyanuric acid thus burnt gives out 1,940 heat units for 1 gram, therefore 250,260 units for 1 equivalent of the acid. The heat of combustion of cyanic acid is obtained by adding to this number, 1,940, the quantity of heat given off by 1 gram of cyanic acid in passing into cyanuric acid, viz. 334 units: hence the heat of combustion of cyanic acid is 2,274 units for 1 gram or 97,780 units for 1 eq. Direct oxidation of cyanic acid by hypochlorous acid to water, carbon dioxide, and nitrogen chloride, gave 2,320 heat units for 1 gram of the acid; and its decomposition by sulphuric acid into ammonia and carbonic acid gives 2,260: mean of all the determinations, 2,290 heat units for 1 gram of cyanic acid. Hence, with the aid of the determinations above given of the heat absorbed and evolved in the molecular transformations of these bodies, it is found that the heat of combustion of cyamelide is 1,880 heat units for 1 gram, and that of cyanuric acid 1,956, which last number differs but little from that directly determined, viz. 1,940.

CYANIC ETHERS. Of these ethers there are two series. Those of the first series, discovered by Wurtz in 1848, are resolved by water, assisted by acids or bases, into carbon dioxide and an alcoholic ammonia; thus:

$$N\left\{\begin{matrix}CO''\\R'\end{matrix}\right. + H^2O = CO^2 + N\left\{\begin{matrix}R'\\H^2\end{matrix}\right.$$

where R' denotes an alcohol-radicle such as methyl or ethyl. These bodies in fact react like alcoholic derivatives of carbimide, $N\left\{\begin{matrix}CO''\\H\end{matrix}\right.$, and may therefore be designated as alcoholic carbimides, pseudocyanates, or isocyanates (they were originally called alcoholic cyanates). They are produced by distilling a mixture of the potassium salts of cyanic acid and methylsulphuric, ethylsulphuric acid, &c.

The second series, discovered by Cloez, consists of ethers which are decomposed by hydration into cyanic or cyanuric acid and an alcohol; thus:

$$\underset{\text{Cyanic ether.}}{O\left\{\begin{matrix}CN\\R\end{matrix}\right.} + \underset{\text{Water.}}{O\left\{\begin{matrix}H\\H\end{matrix}\right.} = \underset{\text{Cyanic acid.}}{O\left\{\begin{matrix}CN\\H\end{matrix}\right.} + \underset{\text{Alcohol.}}{O\left\{\begin{matrix}R'\\H\end{matrix}\right.}$$

or rather perhaps,

$$C\left\{\begin{matrix}N\\OR\end{matrix}\right. + O\left\{\begin{matrix}H\\H\end{matrix}\right. = C\left\{\begin{matrix}N\\OH\end{matrix}\right. + O\left\{\begin{matrix}R\\H\end{matrix}\right.$$

These therefore, though originally called by their discoverer *isocyanates*, are the true alcoholic cyanates or cyanic ethers. They are formed by the action of cyanogen chloride on the sodium-alcohols:

$$C\left\{\begin{matrix}N\\Cl\end{matrix}\right. + NaOR = NaCl + C\left\{\begin{matrix}N\\OR\end{matrix}\right.$$

The difference of structure between the two classes of ethers may be further illustrated by the following formulæ:

$$\underset{\text{Methyl Cyanate.}}{N\equiv C—O—CH^3} \qquad \underset{\text{Methyl Isocyanate or Methyl-carbimide.}}{O=C=N—CH^3}$$

The alcoholic carbimides are fully described in vol. ii. pp. 195–197 as CYANIC ETHERS.

Of the true alcoholic cyanates, the ethyl-compound was discovered by Cloez in 1857 and described under the name *Cyanetholine* (ii. 189); but its properties, together with those of the methylic ether, have since been more completely investigated (Cloez, *Thèses de la Faculté des Sciences de Paris*, août 1866).

Methyl cyanate, $C^2H^3NO = \left.\begin{matrix}CN\\CH^3\end{matrix}\right\}O$, is prepared by dissolving sodium by small portions in pure methyl-alcohol mixed with about twice its weight of anhydrous ether (2 at. sodium to 5 mol. methyl-alcohol), and slowly passing a current of gaseous cyanogen chloride (rather more than the theoretical quantity) to the bottom of the retort containing the mixture. The liquid immediately becomes hot; sodium chloride is precipitated; and on distilling the filtered liquid, methyl cyanate remains as an oil which may be purified by repeated washing with water, and dehydrated in a dry vacuum.

Methyl cyanate is a colourless or slightly yellow liquid having a sp. gr. of 1·1746 at 15°; decomposed by heat into a volatile portion and a solid residue; converted by aqueous potash or ammonia into methyl-alcohol and cyanuric acid; with dry hydrochloric acid gas or the concentrated aqueous acid, it yields methyl chloride and crystallised cyanuric acid.

If the methyl-alcohol used in the preparation of this ether is not quite anhydrous, secondary products are also formed. In one experiment Cloez obtained a white substance insoluble in water, which was precipitated together with the sodium chloride, and when freed from that salt by water, and dissolved in boiling alcohol, formed crystals having the composition of dimethyl-allantoïn, $C^6H^{10}NO^3$ or $C^4H^4(CH^3)^2NO^3$. This substance melts at 225°, and is considerably modified when heated above 230°. Baryta-water decomposes it, eliminating ammonia, and forming a salt which yields a white precipitate with silver nitrate.

Ethyl cyanate, $\left.\begin{matrix}CN\\C^2H^5\end{matrix}\right\}O$, is produced in like manner by the action of cyanogen chloride on a solution of sodium ethylate in absolute alcohol. It is a colourless oily liquid, having a sp. gr. of 1·271 at 15°, an odour like that of sweet oil of wine, and an ethereal bitter taste, with an acrid and persistent after-taste. Heated for several hours to 120°–150°, it gives off, first alcohol, then a mobile liquid which dissolves in the alcohol, and an oily liquid which separates. In the retort there remains a solid yellowish vitreous residue, which when pulverised and treated with hot alcohol, leaves an insoluble portion having nearly the composition of trigenic acid. The oily liquid, washed and dried, distils without alteration at about 195°, and appears by analysis to consist of unaltered ethyl cyanate. This ether is not altered by contact with air; acids gradually separate from it the theoretical quantity of cyanuric acid. With potash or ammonia it yields alcohol and potassium or ammonium cyanurate.

Amyl cyanate, $\left.\begin{matrix}CN\\C^5H^{11}\end{matrix}\right\}O$, is obtained like the preceding compound, but is difficult to purify. Its reactions are similar to those of the methylic and ethylic ethers.

CYANIDE OF HYDROGEN. CNH. *Hydric Cyanide. Hydrocyanic Acid. Prussic Acid. Formonitrile.*—Produced: 1. By direct union of nitrogen with acetylene under the influence of the electric spark: $C^2H^2 + N^2 = 2CNH$ (Berthelot). See ACETYLENE (p. 35).

2. By oxidation of methylamine. When a strong solution of methylamine is set on fire, the hydrogen chiefly burns, and hydrocyanic acid is found in the residual liquid: $NH^2CH^3 + O^2 = 2H^2O + CNH$ (Tollens, *Zeitschr. f. Chem.* [2] ii. 516).

3. By the action of chloroform on ammonia:

$$NH^3 + CHCl^3 = 3HCl + CNH.$$

The reaction is greatly facilitated by adding to the mixture a small quantity of alcoholic potash (Hofmann).

Preparation.—1. The decomposition of mercuric cyanide by hydrochloric acid does not yield more than two-thirds of the theoretical quantity of hydrocyanic acid. This loss is due to the combination of the hydrocyanic acid with the mercuric chloride formed in the reaction, the compound thus produced requiring a rather high temperature to decompose it. This inconvenience may however be obviated by addition of sal-ammoniac, which unites with the mercuric chloride and prevents it from laying hold of the hydrocyanic acid. The process thus modified yields about 95 p. c. of the calculated quantity of hydrocyanic acid (Bussy a. Buignet, *Ann. Ch. Phys.* [4] iii. 232).—2. Hydrocyanic acid may be prepared by distilling a mixture of equal parts of crystallised stannous chloride and mercuric cyanide, the acid passing over, while mercury and stannic oxychloride remain behind (Kletzinsky, *Zeitschr. f. Chem.* [2] ii. 127).

Combination with Water.—Anhydrous prussic acid mixes with water in all proportions; in equal weights, or 3 mol. water to 2 mol. hydrogen cyanide, it forms a true chemical compound. The mixture of the anhydrous acid with water is attended with a lowering of temperature and with a contraction of volume, which attains its maximum, amounting to $\frac{6}{100}$ of the total volume of the mixed liquids, with the proportions just stated (Bussy a. Buignet, *Ann. Ch. Pharm.* [4] iii. 231; *Bull. Soc. Chim.* [2] i. 412).

Reactions.—1. According to Bussy a. Buignet (*J. Pharm.* [3] xliv. 465), the decomposition of the acid which is set up on exposure to light (ii. 218) continues after it is placed in the dark. The acid prepared with yellow prussiate and sulphuric acid is more stable than that obtained with mercuric cyanide and hydrochloric acid.—2. A mixture of hydrocyanic acid vapour and *hydrogen* subjected to the action of the electric spark yields acetylene and nitrogen, the reaction being the inverse of that which takes place in the synthesis of hydrocyanic acid above mentioned; neither of these opposite reactions ever takes place completely (Berthelot, *Compt. rend.* lxvii. 1141).—3. Hydrocyanic acid mixed with *hydrochloric acid* and alcohol, and treated with granulated *zinc*, is converted into methylamine: $CNH + 2H^2 + CH^5N$ (Mendius, *Ann. Ch. Pharm.* cxxxi. 129).—4. When dry mercuric cyanide is heated to dull redness in a stream of gaseous *hydriodic acid*, the hydrocyanic acid at first evolved is resolved, by the further action of the hydriodic acid, into ammonia and marsh gas: $CNH + 3H^2 = NH^3 + CH^4$ (Berthelot, *Jahresb.* 1867, p. 348).—5. Hydrocyanic acid mixed with *hydrogen dioxide* in aqueous solution gradually yields a crystalline precipitate of oxamide: $2CNH + H^2O^2 = C^2H^4N^2O^2$. Oxamide is likewise formed on heating a mixture of potassium cyanide and manganese dioxide with a small quantity of sulphuric acid (Attfield, *Chem. Soc. J.* [2] i. 94).—6. When anhydrous prussic acid is carefully poured, so as not to mix, on phosphorus trichloride, and the liquid is left in an atmosphere of aqueous vapour, it is converted in a short time into a mixture of phosphorous acid, sal-ammoniac, and formic acid (Wehrhane a. Hübner, *Jahresb.* 1864, p. 300).

7. When hydrocyanic acid is heated with acetic acid to 200° in a sealed tube, they partly unite, producing formacetamide: $CHN + C^2H^3O.OH = N(CHO)(C^2H^3O)H$; this however is immediately decomposed into acetamide and carbon monoxide, the latter escaping when the tube is opened: $N(CHO)(C^2H^3O)H = CO + N(C^2H^3O)H^2$. Free hydrocyanic acid is also produced by the decomposition of another portion of the formacetamide: $N(CHO)(C^2H^3O)H = CHN + C^2H^4O^2$ (Gautier, *Ann. Ch. Pharm.* cl. 188).

Detection.—A hot solution of potassium cyanide mixed with *picric acid* assumes a deep blood-red colour due to the formation of picrocyamic acid (iii. 433). Free hydrocyanic acid does not produce this reaction; it must therefore be previously saturated with an alkali. The reaction is said to be more delicate than that with iron salts (C. D. Braun, *Zeitschr. f. anal. Chem.* iii. 464). The deep brown-red colour produced on agitating an alkaline solution of potassio-cobaltous cyanide with air (p. 475) may also be made available for the detection of hydrocyanic acid, the solution being first mixed with excess of alkali, and then with cobalt chloride and tartaric acid (Braun, *loc. cit.*).

COMPOUNDS OF HYDROGEN CYANIDE OR FORMONITRILE WITH HYDRACIDS. *Hydrochloride*, CHN.HCl. *Methenylammonium chloride*, $\left.\begin{matrix}(CH)''' \\ H\end{matrix}\right\}N.Cl$ (Gautier, *Compt. rend.* lxv. 410, 472).—When anhydrous hydrocyanic acid is saturated with dry hydrochloric acid gas at −10°, then heated in a well-closed flask, and left to cool, the liquid after a certain time becomes very hot, and the hydrochloride CHN.HCl separates in crystals. By repeating this treatment several times, the greater part of the hydrocyanic acid may be converted into this compound. To purify the product, it is first heated in the open flask to 40°–50°, then quickly pulverised in a dry atmosphere, and exposed for a few minutes to the same temperature.

It is white, crystalline, inodorous; has a saline and acid taste; dissolves in water, absolute alcohol, and glacial acetic acid, but decomposes quickly in each of these solvents; quite insoluble in ether. It is very hygroscopic and quickly decomposes in contact with the air. Even in a dry vacuum it gradually decomposes and volatilises. When dissolved in water, it is quickly resolved into formic acid and sal-ammoniac. In alsolute alcohol at 30° it is converted into hydrochloride of methenyl-diamine, $N^2(CH)'''H^3.HCl$ (*q.v.*):

$$\underset{\text{Methenylammonium chloride.}}{2\left[\left.\begin{matrix}(CH)''' \\ H\end{matrix}\right\}N.Cl\right]} + \underset{\text{Alcohol.}}{2\left[\left.\begin{matrix}C^2H^5 \\ H\end{matrix}\right\}O\right]} = \underset{\text{Methenyl-diamine hydrochloride.}}{\left.\begin{matrix}(CH)''' \\ H^3\end{matrix}\right\}N^2.HCl} + \underset{\text{Ethyl chloride.}}{C^2H^5Cl} + \underset{\text{Ethyl formate.}}{\left.\begin{matrix}CHO \\ C^2H^5\end{matrix}\right\}O}$$

Glacial acetic acid dissolves methenylammonium chloride, eliminating hydrochloric acid, but the acetate which is probably formed cannot be separated from the excess of acetic acid, since it decomposes at 150°–200° in the manner represented by the following equation:

$$\underset{\text{Methenylammonium acetate.}}{3\left[\left.\begin{matrix}(CH)''' \\ H\end{matrix}\right\}N.OC^2H^3O\right]} = \underset{\text{Formamide.}}{\left.\begin{matrix}CHO \\ H^2\end{matrix}\right\}N} + \underset{\text{Acetamide.}}{\left.\begin{matrix}C^2H^3O \\ H^2\end{matrix}\right\}N} + \underset{\text{Diacetamide.}}{\left.\begin{matrix}(C^2H^3O)^2 \\ H\end{matrix}\right\}N} + 2CO.$$

Chlorine and *bromine* act upon methenylammonium chloride with aid of heat, eliminating hydrochloric or hydrobomic acid, and forming compounds analogous to the propionitrile compounds described by Engler (p. 524). Dry *ammonia* converts it into chloride and cyanide of ammonium. With *potash*, it forms potassium chloride, potassium formate, and ammonia. The alcoholic solution of formonitrile hydrochloride forms with platinic chloride a crystalline precipitate, which however contains salammoniac.

Hydrobromide. CHN.HBr (Gal, *Bull. Soc. Chim.* [2] iv. 431).—Prepared by passing pure dry hydrobromic acid gas into well-cooled anhydrous hydrocyanic acid. The liquid then becomes opaline, and after a while deposits a very light solid mass, which, when freed from excess of acid by standing over caustic potash, forms very hygroscopic granules, nearly insoluble in ether and chloroform, and resolved by water into hydrobromic and hydrocyanic acids, which latter is quickly converted into ammonium formate. According to Gautier, the analysis of this compound leads, not to the formula given by Gal, but to 2CHN.3HBr.

Hydriodide. CHN.HI (Gautier, *Bull. Soc. Chim.* [2] iv. 89).—Produced by passing gaseous hydriodic acid into cooled hydrogen cyanide, or by passing the mixed vapours of the two into a large flask. The white compound, after washing with ether, separates from alcohol in crystals apparently of rhombohedral form; it is inodorous, has a saline bitter taste, and sublimes at 300°–400°, without previous fusion. It is decomposed by water and potash into ammonia, hydriodic acid, and formic acid.

CYANIDES, ALCOHOLIC. Of these compounds there are two classes, both (when containing monatomic alcohol-radicles) being represented by the general formula CNR. In the one class, consisting of the bodies long known as hydrocyanic ethers or nitriles, the alcohol-radicle is in direct union with the carbon; in the other, discovered independently by Hofmann and by Gautier in 1867, and designated as isocyanides, carbylamines, or carbamines, it is combined directly with the nitrogen. The former are analogous in structure to the alcoholic cyanates, the latter to the isocyanates (p 519); thus:

$$N\equiv C{-}R \quad\text{or}\quad C^{iv}\left\{\begin{matrix}N'''\\R'\end{matrix}\right. \qquad\qquad C\equiv N{-}R \quad\text{or}\quad N^{v}\left\{\begin{matrix}C^{iv}\\R'\end{matrix}\right.$$

Cyanides or Nitriles. Isocyanides or Carbamines.*

$$N\equiv C{-}O{-}R \quad\text{or}\quad C^{iv}\left\{\begin{matrix}N'''\\(OR)'\end{matrix}\right. \qquad\qquad O{=}C{=}N{-}R \quad\text{or}\quad N'''\left\{\begin{matrix}(CO)''\\R'\end{matrix}\right.$$

Cyanates. Isocyanates or Carbimides.

The monatomic carbamines are likewise analogous to the carbotriamines, such as guanidine, $N^3\left\{\begin{matrix}C^{iv}\\H^5\end{matrix}\right.$, methyl-carbotriamine or methyluramine, $N^3\left\{\begin{matrix}C^{iv}\\CH^3\\H^4\end{matrix}\right.$, diphenyl carbotriamine or melaniline, $N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^2\\H^3\end{matrix}\right.$, &c.

The most characteristic distinction between the nitriles and the carbamines is afforded by their reaction with hydrating agents (acids and alkalis). The nitriles heated with alkalis are resolved into ammonia and an acid containing the same number of carbon-atoms: *e.g.*,

$$C\left\{\begin{matrix}N\\C^2H^5\end{matrix}\right. + HOK + H^2O = NH^3 + C\left\{\begin{matrix}C^2H^5\\O\\OK\end{matrix}\right.$$

Propionitrile. Potassium propionate.

The carbamines, on the other hand, are attacked with difficulty by alkalis, but are quickly decomposed by aqueous acids, yielding formic acid and the amine corresponding to the alcohol-radicle: *e.g.*,

$$N\left\{\begin{matrix}C\\C^2H^5\end{matrix}\right. + 2H^2O = CH^2O^2 + N\left\{\begin{matrix}H^2\\C^2H^5\end{matrix}\right.$$

Ethylcarbamine. Formic acid. Ethylamine.

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[*] The carbamines are sometimes represented by formulæ containing bivalent carbon, viz. $N'''\left\{\begin{matrix}C'\\R'\end{matrix}\right.$; but their relation to the carbimides is more plainly exhibited by the formulæ above given, the four units of equivalence of the carbon-atom being attached in the one case to the nitrogen alone, and in the other, half to the nitrogen and half to the oxygen.

The carbamines are further distinguished from the nitriles by their lower boiling points, their pungent odour and poisonous character, and by the much greater readiness with which they unite with gaseous hydrochloric acid and other anhydrous haloïd acids.

1. *Nitriles.*

These compounds are formed: 1. By dehydration of the ammonium salts of organic acids containing the corresponding alcohol-radicles: *e.g.*,

$$\underset{\text{Ammonium acetate.}}{C\left\{\begin{matrix}CH^3\\O\\ONH^4\end{matrix}\right.} - 2H^2O = \underset{\text{Acetonitrile.}}{C\left\{\begin{matrix}CH^3\\N\end{matrix}\right.}$$

2. By heating potassium cyanide with an alcoholic iodide or neutral metallic sulphate, or with the potassium salt of methyl-sulphuric, ethyl-sulphuric, and phenyl-sulphuric acids, &c. (ii. 202).

The following reactions are exhibited by the nitriles and not by the carbamines:

α. When heated with *zinc and dilute acids*, they take up 4 at. hydrogen and are converted into primary amines (Mendius, iv.):

$$\underset{\text{Acetonitrile.}}{C\left\{\begin{matrix}N\\CH^3\end{matrix}\right.} + 2H^2 = \underset{\text{Ethylamine.}}{C\left\{\begin{matrix}NH^2\\H^2\\CH^3\end{matrix}\right.}$$

β. They unite directly with 2 at. *bromine*, acetonitrile, for example, forming the compound $C^2H^3NBr^2$ or $C^2H^2BrN.HBr$ (Engler).

γ. They unite with 1 mol. *hydrogen sulphide*, forming sulphuretted amides: *e.g.*,

$$\underset{\text{Benzonitrile.}}{C^7H^5N} + H^2S = \underset{\text{Thiobenzamide.}}{NH^2.C^7H^5S}$$

δ. They unite directly with many *chlorides* of the more electronegative radicles, propionitrile, for example, forming the compounds $C^3H^5N.BCl^3$; $C^3H^5N.COCl^2$; $C^3H^5N.CNCl$; $C^3H^5N.SbCl^3$; $C^3H^5N.AuCl^3$; $(C^3H^5N)^2.PtCl^4$; $(C^3H^5N)^2SiCl^4$; and $(C^3H^5N)^2.TiCl^4$.

ε. With fuming sulphuric acid they form sulpho-acids and disulpho-acids: *e.g.*, acetonitrile yields sulphacetic and disulphometholic acids; thus:

$$\underset{\text{Acetonitrile.}}{C^2H^3N} + 3SO^4H^2 = \underset{\text{Disulphometholic acid.}}{CH^2(SO^3H)^2} + \underset{\text{Acid ammonium sulphite.}}{SO^4H(NH^4)} + CO^2$$

and

$$\underset{\text{Acetonitrile.}}{C^2H^3N} + 2SO^4H^2 + H^2O = \underset{\text{Sulphacetic acid.}}{CH^2\left\{\begin{matrix}SO^3H\\CO^2H\end{matrix}\right.} + SO^4H(NH^4).$$

Methyl Cyanide or Acetonitrile. $C^2H^3N = N{\equiv}C{-}CH^3$.—This compound is fully described (as cyanide of methyl) in vol. ii. p. 257. When quite pure it boils, according to Engler at 76·5° to 77·5° (corr. 77·6°); according to Gautier (*Bull. Soc. Chim.* [2] ix. 2) at 81°–82°. When 6 pts. acetonitrile are heated to 100° in a sealed tube with 1 pt. bromine till the vapours of bromine disappear, and the product is then distilled, acetonitrile bromide, $C^2H^3NBr^2$, passes over (together with excess of acetonitrile) in crystalline crusts, which may be purified by careful sublimation. It forms regular prismatic crystals, probably belonging to the rhombic system. It melts with previous sublimation at 65°, dissolves easily but with decomposition in alcohol, ether, and water, and in contact with moist air gives off hydrobromic acid, and is converted into a mixture of ammonium bromide, ammonium acetate, acetamide, and crystalline di-monobromacetamide, $N(C^2H^2BrO)^2H$. This last compound is gradually deposited from an alcoholic solution of the bromide mixed with water, in thin needle-shaped crystals. Silver nitrate added to an alcoholic solution of acetonitrile-bromide throws down only half the bromine: hence the compound must be regarded as *bromacetonitrile hydrobromide*, $C^2H^2BrN.HBr$. A *dihydrobromide*, $C^2H^3N.2HBr$, is formed by passing dry hydrobromic acid gas through acetonitrile, heating the resulting crystalline mass, and again passing the gas through it. The compound then sublimes and collects in the cooled dry receiver as a yellowish-white crystalline mass. It melts at 47°–50°, begins to sublime at the same temperatures, and is decomposed by water or by exposure to the air, with formation of acetic acid, hydrobromic acid, and ammonia:

$$C^2H^3N.2HBr + 2H^2O = C^2H^4O^2 + NH^4Br + HBr$$

(Engler, *Ann. Ch. Pharm.* cxxix. 24; cxxxiii. 137; cxlii. 65; cxlix. 306; *Jahresb.* 1864, p. 324; 1865, p. 310; 1867, p. 358).

Acetonitrile heated with *sodium* yields, together with sodium cyanide, a base, $C^7H^{13}N^3$, homologous with cyanethine (A. G. Baeyer, *Zeitschr. f. Chem.* [2] iv. 515).

Acetonitrile heated to 200° in a sealed tube with 1 mol. *glacial acetic acid* is partly converted into diacetamide, which passes over on subsequent distillation between 210° and 215° and solidifies in crystals: $C^2H^3N + C^2H^3O.OH = N'''(C^2H^3O)^2H$ or $N^v\begin{cases}(C^2H^3)''' \\ OH \\ C^2H^3O\end{cases}$ (Gautier, *Ann. Ch. Pharm.* cl. 189).

Ethyl Cyanide or Propionitrile. $C^3H^5N = C\begin{cases}N \\ C^2H^5\end{cases}$ (ii. 211).—The great differences of boiling point and other physical properties assigned to this compound by different chemists are doubtless attributable to the difficulty of obtaining it pure; indeed, most of the methods of preparing it appear to yield a mixture of the true nitrile with the isomeric compound, ethyl isocyanide or ethyl-carbamine, to which is due the intolerable odour of the ordinary preparation. Gautier appears to have obtained the purest propionitrile by treating the crude product of the distillation of barium ethylsulphate and potassium cyanide with an acid (which decomposes the ethyl-carbamine), then agitating it with mercuric oxide, distilling, and treating the distillate with a large quantity of calcium chloride, which removes a compound of the nitrile with alcohol, leaving the nitrile itself to be further purified by rectification. Propionitrile thus prepared has an alliaceous odour and boils at 88·5°.

Action of Bromine and Hydrobromic Acid (Engler, *loc. cit.*).—When hydrobromic acid gas is passed in excess into propionitrile, a yellow crystalline mass is formed consisting of the hydrobromide $C^3H^5N.2HBr$. It melts at 50°–55°, sublimes at a slightly higher temperature, and decomposes slowly in contact with dry, quickly in contact with moist air, yielding propionic acid. Its decomposition with water is represented by the equation:

$$C^3H^5N.2HBr + 2H^2O = C^3H^6O^2 + NH^4Br + HBr.$$

According to Gautier, anhydrous *hydriodic acid* also unites directly with propionitrile.

Bromopropionitrile Hydrobromide, $C^3H^4BrN.HBr$, is prepared, like the corresponding compound of acetonitrile, by heating 10 pts. propionitrile with 1 pt. bromine to 100° in a sealed tube. The crystalline product purified by sublimation melts at 64°, and begins to sublime at 72°, with partial decomposition, in stellate groups of crystalline crusts. It is decomposed by water, like bromacetonitrile hydrobromide, yielding *dimonobromopropionamide*, $N(C^3H^4BrO)^2H$.

Action of Hydrochloric Acid and Chlorine.—Dry hydrochloric acid gas is dissolved by propionitrile, but without at first appearing to enter into definite combination, even when the solution is heated to 100° in sealed tubes; if, however, it be left to itself in a sealed vessel for a month, crystals of a hydrochloride, $C^3H^5N.HCl$, are formed apparently belonging to the monoclinic system. This compound dissolves very sparingly in ether, but freely in alcohol, chloroform, and water. Its aqueous solution is comparatively little altered by boiling; but when left to itself it is gradually converted into sal-ammoniac and propionic acid: $C^3H^5N.HCl + 2H^2O = NH^4Cl + C^3H^6O^2$. The hydrochloride softens at 95°, melts at 121°, and quickly becomes uncrystallisable. When strongly heated in the air, it burns, leaving scarcely a trace of carbon (Gautier, *Compt. rend.* lxiii. 921).

Respecting the action of chlorine on propionitrile, see vol. iv. p. 736.

Action of Acetic Acid (Gautier, *Ann. Ch. Pharm.* cl. 189).—Propionitrile heated with excess of acetic acid in a sealed tube for fifteen to twenty hours is in great part converted into propionic acid and triacetodiamide:

$$2C^3H^5N + 3(C^2H^3O.OH) + H^2O = 2(C^3H^5O.OH) + N^2(C^2H^3O)^3H^3.$$

The portion of the resulting liquid which passes over on distillation between 212° and 217° becomes filled in the course of twenty-four hours with long silky needles of triacetodiamide. This compound is soluble in water, alcohol, and ether, is converted into ammonium acetate by heating with water to 200°, and resolved by potash into ammonia and acetic acid.

to dry distillation, yields amidobenzonitrile (together with gases, water, ammonium carbonate, and ammonium cyanide), as an oil, which may be purified by solution in hydrochloric acid, treatment with animal charcoal, precipitation with ammonia, and crystallisation (Griess, *Zeitschr. f. Chem.* [2] iv. 725).

Amidobenzonitrile crystallises in colourless needles or prisms, melting at 53° (Griess), at 52°, and boiling at 288°-290° (Hofmann). It dissolves easily in alcohol, ether, and boiling water, but is nearly insoluble in cold water (Griess). The *sulphate* and *nitrate* crystallise well, the latter in four-sided tables; the *picrate* is very sparingly soluble (Hofmann). The *hydrochloride* $C^7H^6N^2.HCl$ forms rhombic tables easily soluble in alcohol and in cold water; the *platinochloride* $2(C^7H^6N^2.HCl).PtCl^4$, yellow, four-sided tables, easily soluble in water. The *argentonitrate*, $C^7H^6N^2.AgNO^3$, obtained by adding silver nitrate to the aqueous or alcoholic solution of the base, forms white laminæ. With *bromine-water* the aqueous solution of the base gives a brominated compound crystallising in needles (Griess).

Amidobenzonitrile boiled with strong *hydrochloric acid* yields sal-ammoniac and amidobenzoic hydrochloride, $C^7H^7NO^2.HCl$. With *chloroform* and *alkalis* it yields the intolerably smelling formonitrile, $C^8H^4N^2$, which is resolved by acids into formic acid, amidobenzoic acid, and ammonia, whereas the isomeric formonitrile of phenylenediamine is resolved by similar treatment into formic acid and phenylenediamine (Hofmann).

When nitrobenzonitrile is treated with *ammonium sulphide*, a sulphuretted base, $C^7H^8N^2S^2$, containing the elements of amidobenzonitrile and hydrogen sulphide, is produced, which crystallises from boiling water in white shining needles, easily soluble in alcohol and ether, and forming a crystalline hydrochloride and platinochloride. At a few degrees above 100° it is resolved, though not completely, into H^2S and $C^7H^6N^2$. This base has the constitution of thiobenzylene-diamide, $N^2(C^7H^4S)''H^4$, and is isomeric with sulphocarbonyl-phenyl-diamide, $N^2(CS)''(C^6H^5)H^3$, produced by the action of ammonia on phenyl sulphocyanate (Hofmann, *Proc. Roy. Soc.* x. 599).

Paramidobenzonitrile is obtained by the action of tin and hydrochloric acid, or better of zinc and hydrochloric acid, on paranitrobenzonitrile, and separates, on saturating the product with soda and evaporating, as an oil which solidifies on cooling, and may be purified by recrystallisation from aqueous alcohol. It dissolves easily in alcohol and ether, sparingly in water, and crystallises from a mixture of 1 pt. alcohol and 1 pt. water, by slow cooling, in colourless needles melting at 74°. It dissolves easily in acids, forming for the most part crystallisable salts. The *hydrochloride* $C^7H^6N^2.HCl$ forms thin laminar colourless crystals, easily soluble in water, melting when heated, and decomposing at a higher temperature. The *platinochloride* $2(C^7H^6N^2.HCl).PtCl^4$ forms small crystalline needles. By prolonged heating with zinc and hydrochloric acid, it is decomposed, yielding sal-ammoniac and benzylamine (Engler, *Zeitschr. f. Chem.* [2] iv. 615; *Ann. Ch. Pharm.* cxlix. 302).

Paranitrobenzonitrile treated with *ammonium sulphide* yields a base, $C^7H^8N^2S$, isomeric with that obtained by Hofmann from nitrobenzonitrile. It crystallises from alcohol in yellowish white stellate masses; melts at 170°; dissolves in hydrochloric acid, and may be separated therefrom by fixed alkalis (Engler).

Paranitrobenzonitrile is slowly reduced by sodium-amalgam, yielding a weak base, probably consisting of the azo-compound $N(C^7H^4)N$ (Engler).

Naphthyl Cyanide. $C^{11}H^7N = C\left\{\begin{matrix}N\\C^{10}H^7\end{matrix}\right.$ (Hofmann, *Compt. rend.* lxiv. 387; lxvi. 473; lxvii. 547).—Produced: 1. By distilling naphthylamine with oxalic acid. The reaction takes place by two stages: the oxalic acid first splits up into water, carbon dioxide, and carbon monoxide, which latter fixes itself upon the naphthylamine, converting it into naphthyl-formamide; and the naphthyl-formamide is then resolved by the heat into water and naphthyl cyanide (Hofmann).

$$\underset{\text{Naphthylamine.}}{N\left\{\begin{matrix}C^{10}H^7\\H\\H\end{matrix}\right.} + \underset{\text{Oxalic acid.}}{(C^2O^2)''(OH)^2} = CO^2 + H^2O + \underset{\text{Naphthyl-formamide.}}{N\left\{\begin{matrix}C^{10}H^7\\COH\\H\end{matrix}\right.}$$

and

$$N\left\{\begin{matrix}C^{10}H^7\\COH\\H\end{matrix}\right. = H^2O + C\left\{\begin{matrix}N\\C^{10}H^7\end{matrix}\right..$$

The distillate thus obtained is a mixture of naphthyl cyanide, naphthyl-formamide, naphthyloxamide, naphthylamine oxalate, naphthalene, and water. It is treated with a current of steam, which carries along with it a considerable quantity of a brown opaque oil heavier than water. On separating this oil from the water by agitation with ether, evaporating the ether, and distilling the residue, naphthalene passes over at 218°–220°, and naphthyl cyanide at 290°–300°, as a light yellow liquid, which solidifies to a crystalline mass when left for some time in a cold room, more quickly in a freezing mixture, and when once solidified does not return to the liquid state at ordinary temperatures. It may be obtained perfectly pure by recrystallising it several times from alcohol, in which it is very soluble, and finally precipitating it from the alcoholic solution by water. It then separates as an oil which solidifies in a few minutes (Hofmann).

2. By distilling a mixture of cyanide and naphthylsulphite of potassium (Merz, *Bull. Soc. Chim.* ix. 335; x. 47):

$$KCN + (SO)''\left\{\begin{matrix}OC^{10}H^7\\OK\end{matrix}\right. = SO''\left\{\begin{matrix}OK\\OK\end{matrix}\right. + C^{10}H^7CN.$$

Naphthyl cyanide is heavier than water, melts at 35·5°, and boils at 296° (corr.). When boiled with *alcoholic soda* it gives off only traces of ammonia; but on adding water to the mixture, crystals are deposited consisting of menaphthoxylamide, $C^{11}H^9NO$ = naphthyl cyanide + 1 mol. water. The menaphthoxylamide, as soon as it is formed, is decomposed by the soda, with evolution of ammonia and formation of menaphthoxylic acid, $C^{10}H^7.CO^2H$, an acid related to naphthalene in the same manner as benzoic acid to benzene:

$$\underset{\text{Naphthyl cyanide.}}{C\left\{\begin{matrix}C^{10}H^7\\N\end{matrix}\right.} + H^2O = \underset{\text{Menaphthoxylamide.}}{C\left\{\begin{matrix}C^{10}H^7\\O''\\NH^2\end{matrix}\right.}$$

$$\underset{\text{Menaphthoxylamide.}}{C\left\{\begin{matrix}C^{10}H^7\\O''\\NH^2\end{matrix}\right.} + NaOH = NH^3 + \underset{\text{Sodium menaphthoxylate.}}{C\left\{\begin{matrix}C^{10}H^7\\O''\\ONa\end{matrix}\right.}$$

Naphthyl cyanide combines but slowly with nascent hydrogen; but when heated to 100° with alcoholic solution of ammonium sulphide it readily takes up H^2S, and is converted into menaphthothiamide, $C^{11}H^9NS$ (Hofmann).

2. *Alcoholic Isocyanides* or *Carbamines.*

These ethers are produced: 1. By distilling a monamine with chloroform (Hofmann): *e.g.*,

$$\underset{\text{Aniline.}}{N'''\left\{\begin{matrix}C^6H^5\\H^2\end{matrix}\right.} + \underset{\text{Chloroform.}}{CHCl^3} = 3HCl + \underset{\text{Phenyl Isocyanide.}}{\dot{N}^{v}\left\{\begin{matrix}C^{iv}\\C^6H^5\end{matrix}\right.}$$

2. By treating 1 mol. of an alcoholic iodide with 2 mol. silver cyanide, a double cyanide of silver and the alcohol-radicle is then formed; and on distilling this compound with a very strong aqueous solution of potassium cyanide, a double cyanide of silver and potassium is formed, and the isocyanide of the alcohol-radicle distils over; it may then be dried over calcium chloride and rectified. By this reaction Gautier has prepared the isocyanides of methyl, ethyl, isopropyl, and butyl. The ethyl-compound was obtained some years ago in an impure state by E. Meyer, by distilling potassium-silver cyanide with potash (ii. 212).

The isocyanides are also formed in small quantity in the preparation of the nitriles, and to them is due the intolerable odour of the crude distillates.

Methyl Isocyanide or **Methyl-carbamine.** $CH^3{-}N{\equiv}C$ or $N^{v}\left\{\begin{matrix}C^{iv}\\CH^3\end{matrix}\right.$ (Gautier, *Compt. rend.* lxv. 468, 862; lxvi. 1214).—Prepared, as above described, by heating 2 mol. silver cyanide with 1 mol. methyl iodide to 130°–140° in a close vessel, and decomposing the resulting double cyanide with potash. When dried with calcium chloride and purified by rectification, it is a colourless mobile liquid having a specific gravity of 0·7557 at 14°, boiling at 58°–59°, not solidifying at −45°. It has a powerful odour, like that of phosphorus and of artichokes. Its vapours are acrid and very deleterious, almost immediately producing nausea, vertigo, headache, and depression. Water dissolves about $\frac{1}{10}$ pt. of it at 15°. When heated with water in a sealed tube, it is resolved into formic acid and methylamine:

$$N\left\{\begin{matrix}C\\CH^3\end{matrix}\right. + 2H^2O = CH^2O^2 + N\left\{\begin{matrix}CH^3\\H^2\end{matrix}\right. .$$

With dry acids (pure hydrogen-salts) it unites immediately, saturating them completely like ammonia, and forming crystallisable salts. The hydrochloride and hydrobromide are very easily obtained by directing the dry gaseous acids on the surface of the liquid kept very cool. The combinations with oxygen-acids are more difficult to obtain, on account of the violence of the reaction. All these salts are decomposed by water, with production of formic acid and methylamine. *Alcoholic iodides* combine with methyl isocyanide at ordinary temperatures, whereas acetonitrile does not unite with these bodies at any temperature between 0° and 200°.

Methyl-carbamine is very easily oxidised. When it is brought in contact with *mercuric oxide* in a cooled vessel, and the mixture is then gradually heated in a water-bath to 40°–50°, metallic mercury separates and methyl isocyanate or methyl-carbimide distils over:

$$N\left\{\begin{matrix}C\\CH^3\end{matrix}\right. + HgO = Hg + N\left\{\begin{matrix}CO\\CH^3\end{matrix}\right. .$$

A considerable portion of this body is, however, converted into a compound of methyl cyanurate and formamide, which may be obtained in crystals by heating the liquid remaining in the flask to 160°, and exhausting with boiling alcohol. The reaction is:

$$\underset{\text{Methyl carbamine.}}{4N\left\{\begin{matrix}C\\CH^3\end{matrix}\right.} + O^5 = \underset{\text{Methyl cyanurate.}}{N^3\left\{\begin{matrix}(CO)^3\\(CH^3)^3\end{matrix}\right.} . \underset{\text{Formamide.}}{N\left\{\begin{matrix}CHO\\H^2\end{matrix}\right.} + CO.$$

This compound melts and partially sublimes at 175°, but decomposes when heated above 250°. It dissolves in water, alcohol, and ether, and crystallises from water in beautiful laminæ. Heated with potash to 200° it gives off a little ammonia. An ethereal solution of methyl-carbamine treated in the manner above described yields, in addition to the preceding products, a crystalline body which melts at 163°, boils at 168° under a pressure of 24 mm., and consists of $N^3\left\{\begin{matrix}(CO)^3\\(CH^3)^3\end{matrix}\right. . N\left\{\begin{matrix}(CHO)^2\\H\end{matrix}\right.$. Similar products are obtained by oxidising methyl-carbamine in ethereal solution with silver oxide; but they remain at first in combination with that oxide. On evaporating the ether, a white substance remains, which quickly yields metallic silver and further products of oxidation (Gautier, *Compt. rend.* lxvii. 804; *Zeitschr. f. Chem.* [2] iv. 675).

Ethyl Isocyanide or **Ethyl-carbamine.** $N\left\{\begin{matrix}C\\C^2H^5\end{matrix}\right.$ (Gautier, *loc. cit.*).—Prepared like the preceding. Boils between 78° and 79°. Sp. gr. 0·7588 at +4°. Does not solidify at −68°. It unites with acids like methyl-carbamine, forming crystallisable salts. Heated to 180° with *water* or an alkaline solution, it yields formic acid and ethylamine. The hydrochloride boiled with potash yields the same products, together with ethyl-formamide:

$$N\left\{\begin{matrix}C\\C^2H^5\end{matrix}\right. .HCl + KOH = KCl + N\left\{\begin{matrix}C^2H^5\\COH\\H\end{matrix}\right. .$$

Ethyl-carbamine is violently oxidised by *silver oxide*, with formation of ethyl cyanate, and a crystalline body, $C^{13}H^{25}N^5O^3$, soluble in alcohol and boiling above 200°:

$$5NC(C^2H^5) + O^6 = C^{13}H^{25}N^5O^4 + 2CO.$$

When ethyl-carbamine dissolved in 4 vol. ether is oxidised by *mercuric oxide*, the chief products are a crystallisable body, $C^9H^{22}N^4O^2$, melting at 112°, and liquid formamide:

$$5N\left\{\begin{matrix}C\\C^2H^5\end{matrix}\right. + 8HgO = C^9H^{22}N^4O^2 + N\left\{\begin{matrix}COH\\H^2\end{matrix}\right. + 5CO + Hg^8.$$

The crystalline body may be regarded as a compound of ethyl-formamide with ethyl-carbodiamine:

$$C^9H^{22}N^4O^2 = 2N\left\{\begin{matrix}COH\\C^2H^5\\H\end{matrix}\right. + \begin{matrix}N^v\\|\\N^v\end{matrix}\left\{\begin{matrix}C^{iv}\\C^2H^5\\H^3\end{matrix}\right. .$$

Ethyl-carbamine and methyl-carbamine heated in sealed tubes to 190° remain for the most part unaltered; but on opening the tubes and distilling off the more volatile portion, an oily liquid remains, which explodes violently when more strongly heated. Gautier regards these liquids as polymerides of the carbamines.

Isopropyl Isocyanide or **Isopropyl-carbamine,** $C^4H^7N = N\left\{\begin{matrix}C\\ CH(CH^3)^2\end{matrix}\right.$ (Gautier, *Compt. rend.* lxvii. 723), is produced by acting upon silver cyanide with isopropyl iodide, and decomposing the double cyanide $NC(C^3H^7).NCAg$ by boiling with a concentrated aqueous solution of potassium cyanide. It is a liquid smelling like the carbamines previously described, soluble in alcohol and ether, very slightly soluble in water, having a sp. gr. of 0·7596 at 0°, boiling at 87°, not solidifying at −68°. It unites readily with dry haloïd acids, forming crystallisable salts. Treated with aqueous hydrochloric acid, it is transformed, by two successive degrees of hydration, first into isopropyl-formamide, then into isopropylamine formate:

$$N\left\{\begin{matrix}C\\ C^3H^7\end{matrix}\right. + H^2O = N\left\{\begin{matrix}COH\\ C^3H^7.\\ H\end{matrix}\right.$$

$$N\left\{\begin{matrix}C\\ C^3H^7\end{matrix}\right. + 2H^2O = N(C^3H^7)H^2.CH^2O^2.$$

Butyl Isocyanide or **Butyl-carbamine,** $C^5H^9N = N\left\{\begin{matrix}C\\ C^4H^9\end{matrix}\right.$, prepared like the preceding, is a colourless liquid, having an offensive odour, nearly insoluble in water, boiling at 114°–117°, and having a sp. gr. of 0·7833 at 0°. When cooled to −66° it does not crystallise, but becomes pasty and opaque. Water and mineral acids act upon it less violently than on the preceding carbamines. Heated with aqueous acids it takes up 2 mol. water and is completely transformed into butylamine and formic acid (Gautier, *Bull. Soc. Chim.* [2] xi. 211; *Zeitschr. f. Chem.* [2] v. 445).

Amyl Isocyanide or **Amyl-carbamine.** $C^6H^{11}N = N\left\{\begin{matrix}C\\ C^5H^{11}\end{matrix}\right.$ (Hofmann, *Ann. Ch. Pharm.* cxliv. 114; *Jahresb.* 1867, p. 363).—Prepared by distilling an alcoholic solution of amylamine with chloroform and potash:

$$CHCl^3 + N\left\{\begin{matrix}C^5H^{11}\\ H^2\end{matrix}\right. = 3HCl + N\left\{\begin{matrix}C\\ C^5H^{11}\end{matrix}\right.$$

Purified like the phenyl compound. It may also be obtained, like the preceding carbamines, by decomposing silver cyanide with amyl iodide, &c. It is a colourless liquid having a pungent odour of amyl alcohol and prussic acid together, boils at 137° (capronitrile at 146°). Its vapour produces an intensely bitter taste upon the tongue and a suffocating sensation in the throat. It is violently attacked by hydrochloric acid, the reaction taking place by several stages, and finally resulting, after the liquid has been heated to the boiling point, in the production of amylamine and formic acid.

Phenyl Isocyanide or **Phenyl-carbamine.** $C^7H^5N = N\left\{\begin{matrix}C\\ C^6H^5\end{matrix}\right.$ (Hofmann, *loc. cit.*).—This compound, isomeric with benzonitrile, is obtained by distilling a mixture of aniline, chloroform, and alcoholic potash; rectifying the pungent-smelling distillate; treating the portion which goes over after the water and alcohol, with oxalic acid to precipitate the aniline contained in it; dehydrating the residual brown oil with potassium hydrate, and rectifying it.

Pure phenyl-carbamine thus obtained is a mobile liquid, blue by reflected, green by transmitted light, and retaining these colours even after rectification in a current of steam. Its odour is pungently aromatic, and at the same time like that of prussic acid. Its vapour acts on the throat and tongue like that of the amyl-compound, but less strongly. It boils at 160° (benzonitrile at 191°), but with partial decomposition, the temperature quickly rising to 230°, and a brown inodorous oil distilling over, which solidifies in the crystalline form on cooling. It unites very easily with metallic cyanides (benzonitrile unites with them but slowly), forming, with silver cyanide in particular, a beautifully crystallised compound. It is scarcely attacked by alkalis, but is easily decomposed even by dilute acids, and with great evolution of heat by concentrated acids, yielding, as ultimate products, formic acid and aniline, with methenyl-diphenyldiamine and phenyl-formamide as intermediate products; thus:

$$(1)\quad \underset{\text{Phenyl-carbamine.}}{2NC(C^6H^5)} + 2H^2O = \underset{\text{Formic acid.}}{CH^2O^2} + \underset{\text{Methyl-diphenyl-diamine.}}{N^2(CH)'''(C^6H^5)^2H}$$

$$(2)\quad \underset{\text{Methenyl-diphenyl-diamine.}}{N^2(CH)'''(C^6H^5)^2H} + H^2O = \underset{\text{Phenyl-formamide.}}{N(CHO)(C^6H^5)H} + \underset{\text{Aniline.}}{N(C^6H^5)H^2}$$

$$(3)\quad \underset{\text{Phenyl-formamide.}}{N(CHO)(C^6H^5)H} + H^2O = \underset{\text{Formic acid.}}{CH^2O^2} + \underset{\text{Aniline.}}{N(C^6H^5)H^2}$$

CYANIDES, METALLIC. It cannot at present be decided whether these salts are analogous in constitution to the nitriles $N{\equiv}C—R'$, or to the carbamines $C{\equiv}N—R$; their conversion by the action of water into ammonia and a salt of formic acid may be explained with equal facility on either view. Silver cyanide heated with ethyl iodide yields ethyl carbamine, $N\left\{\begin{matrix}C^{iv}\\C^2H^5\end{matrix}\right.$; and potassium cyanide similarly treated yields chiefly propionitrile, $C\left\{\begin{matrix}N'''\\C^2H^5\end{matrix}\right.$: whence it might be inferred that some metallic cyanides are analogous to the nitriles, others to the carbamines. It is possible also that the same metallic cyanide may exist sometimes in one modification, sometimes in the other; indeed, the propionitrile obtained from potassium cyanide is always more or less mixed with ethyl-carbamine (p. 524). Similar remarks apply to hydrogen cyanide, which is usually regarded as formonitrile, $(CH)'''N$, but may perhaps be also capable of assuming the form of carbamine, NCH.

AMMONIUM CYANIDE, NH^4CN, is formed in the combustion of coal-gas which has passed through aqueous ammonia. If the gas be burnt in a long tube and the condensed products passed into water, a solution of ammonium cyanide is obtained; if the flame be made to pass over potash-solution· or milk of lime, the liquid, after a few minutes, is found to contain considerable quantities of cyanide; and on shaking up the potash-solution with finely divided iron, potassium ferrocyanide is obtained (De Romilly, *Compt. rend.* lxv. 865). When dry ammonia-gas is passed over pure wood-charcoal heated in a glass tube to the highest temperature of a gas-furnace, a small quantity of ammonium cyanide is formed, together with a mixture of nitrogen and hydrogen gas (Weltzien, *Ann. Ch. Pharm.* cxxxii. 224).

BARIUM CYANIDES.—Barium platinocyanide, $BaPtCy^4$, is produced by the mutual action of platinous or platinic chloride with barium carbonate and dilute hydrocyanic acid. With platinic chloride the reaction is:

$$3BaCO^3 + PtCl^4 + 4HCy = BaPtCy^4 + 2BaCl^2 + 2H^2O + 3CO^2 + O.$$

Double cyanides of barium with other metals are formed in like manner by the mutual action of barium carbonate, hydrocyanic acid, and the nitrates, carbonates, cyanides, acetates, or, best of all, the soluble sulphates of the several metals (Weselsky, *J. pr. Chem.* ciii. 566).

·**CHROMIUM CYANIDES.**—On the preparation and properties of the chromicyanides $6M'Cy.Cr^2Cy^6$ and $3M''Cy^2.Cr^2Cy^6$ (ii. 205), see Kaiser (*Ann. Ch. Pharm. Suppl.* iii. 163; *Jahresb.* 1864, p. 302) and Stridsberg (*ibid.* p. 304). A solution of potassium chromicyanide treated with sodium-amalgam is immediately coloured red, in consequence of reduction to *potassium chromocyanide*, $4KCy.Cr''Cy^2$. The solution of this latter salt is decomposed by dilution and by heating. It gives a red-brown precipitate with zinc salts, green with chromic salts, red with cobalt salts, and green with manganous salts (Descamps).

COBALT CYANIDES (Descamps, *Compt. rend.* lxvii. 330).—Cobalt forms two series of double cyanides analogous to the ferro- and ferri-cyanides. *Potassium cobaltocyanide*, $K^4Co''Cy^6$, is formed in the first instance on dissolving cobaltous cyanide in aqueous potassium cyanide; but under ordinary circumstances it is immediately converted into the cobalticyanide. When a concentrated solution of potassium cyanide is poured into a vessel containing cobaltous cyanide, the latter being in excess, and all rise of temperature avoided, a greenish solution of cobaltous cyanide in potassium cyanide is formed, which when left to itself, becomes red on the surface from formation of potassium cobaltocyanide, and deposits a green powder consisting of potassio-cobaltous cobaltocyanide. If on the other hand a slight excess of potassium cyanide be added, a deep red solution of potassium cobaltocyanide is quickly produced; it is necessary however to keep the liquid cool; otherwise the cobaltocyanide is immediately converted into colourless cobalticyanide, with evolution of hydrogen. By quickly evaporating the solution in a vacuum, a few red needles of the cobaltocyanide are obtained, but the greater part suffers decomposition. A better method is to precipitate the salt from its aqueous solution with alcohol, and wash it with the same liquid; if it be then redissolved in water, a more stable and crystallisable solution will be obtained.

Potassium cobaltocyanide is red, very deliquescent, insoluble in alcohol and ether; alterable on exposure to air, but more permanent under alcohol. Its solution is decomposed by boiling into potassium cobalticyanide and cobalt sesquioxide; this decomposition is much accelerated by a trace of potash, and is almost instantly brought about in dilute solutions by addition of potassium cyanide. The cobaltocyanides of sodium and barium are also red. The solution of the potassium salt forms a reddish precipitate with zinc salts; flesh-coloured with manganous sulphate; yellow with lead acetate; orange-coloured with mercuric salts; rose-coloured with cadmium salts. On mixing a concentrated solution of cobalt nitrate with a concentrated alkaline solution of cobaltous cyanide, a green precipitate is formed consisting of potassio-cobaltous cobaltocyanide, $Co''K^2Cy^4.Co''Cy^2$. The same compound is formed on pouring a solution of potash on cobaltous cyanide. It is insoluble in water, permanent in the dry state, and dissolves very easily in potassium cyanide, reproducing potassium cobaltocyanide.

The colourless solution of potassium *cobalticyanide* treated with sodium-amalgam is quickly converted into the red cobaltocyanide (Descamps).

Cobalticyanides. $M^6(Co^2)^{vi}Cy^{12}$.—Several of these salts are described in vol. ii. pp. 205, 206. The *barium salt* $Ba^3Co^2Cy^{12} + 20H^2O$ may be prepared by treating a mixture of cobaltous sulphate and barium carbonate with hydrocyanic acid; and in this salt the barium is easily replaced by other metals or by compound radicles (*e.g.* phenylammonium and tolylammonium), by treating the solution with the corresponding sulphates. In this manner the following salts have been obtained:

$Na^6Co^2Cy^{12} + 4H^2O$ . . .	Large crystals.
$(NH^4)^6Co^2Cy^{12}$	Colourless tables, or with a faint tinge of yellow.
$(C^6H^8N)^6Co^2Cy^{12}$	Crystals rarely quite colourless, more frequently with the aspect of smoky topaz.
$(C^7H^{10}N)^6Co^2Cy^{12}$	Nearly colourless crystals resembling nitre.
$Sr^3Co^2Cy^{12} + 20H^2O$ . . .	Very large crystals, easily soluble in water.

(Weselsky, *Wien. Acad. Ber.* lx. 261; *Chem. Centr.* 1870, p. 92.)

Cobalticyanides containing three metals are obtained by leaving mixed solutions of the preceding cobalticyanides to crystallise. On evaporating, the triple salt separates out if it is less soluble than the mixed double salts, or remains in the mother-liquor in the contrary case, after the latter have crystallised out. These triple salts likewise crystallise with very great facility, forming large and beautiful crystals. The following have been prepared:

$(NH^4)^4Na^2Co^2Cy^{12}$
$Ca^2(NH^4)^2Co^2Cy^{12} + 10H^2O$
$Ca^2K^2Co^2Cy^{12} + 18H^2O$
$Sr^2(NH^4)^2Co^2Cy^{12} + 20H^2O$
$Sr^2K^2Co^2Cy^{12} + 18H^2O$

$Ba^2(NH^4)^2Co^2Cy^{12} + 22H^2O$
$Ba^2K^2Co^2Cy^{12} + 22H^2O$
$Ba^2Li^2Co^2Cy^{12} + 30H^2O$

$$\left.\begin{matrix}(C^7H^{10}N)^4\\(C^6H^8N)^2\end{matrix}\right\}Co^2Cy^{12} + 3H^2O$$

The last salt is prepared by mixing one half of a solution of barium cobalticyanide with aniline sulphate, the other half with toluidine sulphate, mixing the filtered solutions, and leaving the mixture to evaporate: it forms groups of large efflorescent crystals having the colour of beryl (Weselsky).

A solution of barium cobalticyanide mixed with excess of baryta-water and left to evaporate under the air-pump, yields the compound $Ba^3Co^2Cy^{12}.BaH^2O$, in somewhat unstable crystals which absorb carbonic acid from the air. A mixed solution of cobalticyanide and chloride of barium yields the salt $Ba^3Co^2Cy^{12}.BaCl^2 + 16H^2O$, in tabular crystals more stable than the preceding compound. A warm solution of phenylammonium-cobalticyanide saturated with aniline becomes turbid on cooling, from separation of the excess of aniline, and the clarified liquid evaporated under the air-pump yields the compound $(C^6H^8N)^6Co^2Cy^{12}.2(C^6H^9NO)$, in groups of faintly coloured bulky prisms, somewhat readily decomposible, the aniline being eliminated by boiling (Weselsky).

COPPER CYANIDES.—*Cupric Cyanide*, $CuCy^2$, can be obtained in the pure state only by treating recently precipitated cupric hydrate with hydrocyanic acid. It is an easily alterable, amorphous, green powder, which gives off half its cyanogen at a temperature below 100°, leaving white cuprous cyanide, Cu^2Cy^2. The latter melts at a dull red heat, decomposes at a bright red heat, quickly turns dark blue in ammoniacal solution, and unites with the cyanides of the alkali-metals, forming double salts, $MCy.Cu^2Cy^2$, sparingly soluble in cold water, and easily decomposed by acids, with separation of cuprous cyanide. The potassium salt and the ammonium salt (the latter obtained by spontaneous evaporation of a solution of cuprous cyanide in ammonium cyanide) crystallise in anhydrous rectangular prisms, the aqueous solution of which is precipitated by metallic salts, with formation of analogous double cyanides. Mercuric salts give a white, silver salts a bluish-grey, cupric salts a green precipitate, consisting of cuproso-cupric cyanide, $CuCy^2.2Cu^2Cy^2$ (Lallemand, *Bull. Soc. Chim.* [2] ii. 271; *Compt. rend.* lx. 1142; *Jahresb.* 1864, p. 300; 1865, p. 391). According to Schiff a. Bech. (*Bull. Soc. Chim.* [2] iii. 373), an ammoniacal solution of the white ammoniacal compound $2NH^3.Cu^2Cy^2$ boiled in an open vessel deposits on cooling shining violet crystals of the compound $N^2H^6CuCy^2.2N^2H^6Cu^2Cy^2$.

GOLD CYANIDES.—*Potassio-auric iodocyanide*, $KAu'''Cy^2I^2$, is easily formed by the action of iodine on potassio-aurous cyanide, $KAu'Cy^2$, and may be crystallised from warm water, in which it is much more soluble than in cold water. It forms brown, shining, long capillary needles. The corresponding *barium salt* forms brown highly lustrous scales. The corresponding *bromine-compounds* are reddish-yellow; the *chlorine-compounds* nearly colourless. The double aurocyanides behave with various reagents in the same manner as the corresponding platinic compounds (p. 536); thus the copper salt $Cu''Au^2Cy^4$ takes up bromine without decomposition (Blomstrand, *Zeitschr. f. Chem.* [2] v. 439).

IRON CYANIDES.—The general formulæ of the double cynnides of iron (Fe = 56) containing monatomic and diatomic metals may be illustrated by the following examples:

$$\text{Ferrocyanides}\begin{cases}K^4Fe''Cy^6 & = 4KCy.Fe''Cy^2\\ Ba''^2Fe''Cy^6 & = 2Ba''Cy^2.Fe''Cy^2\end{cases}$$
$$\text{Ferricyanides}\begin{cases}K^6(Fe^2)^{vi}Cy^{12} & = 6KCy.Fe^2Cy^6\\ Ba''^3(Fe^2)^{vi}Cy^{12} & = 3Ba''Cy^2.Fe^2Cy^6\end{cases}$$

Ferrocyanides.—The *ammonio-nickel ferrocyanide*, which, according to Reynose, is deposited in violet needles from the solution of nickel ferrocyanide in excess of ammonia, has, according to Gintl (*Zeitschr. f. Chem.* [2] iv. 525), the composition $Ni^2FeCy^6.12NH^3 + 9H^2O$. When exposed to the air it gives off ammonia, and is converted into a light green powder, $Ni^2FeCy^6.2NH^3 + 9H^2O$; and at about 100°, into a dark brown powder, $Ni^2FeCy^6.2NH^3 + 4H^2O$, which at higher temperatures undergoes complete decomposition, giving off water and ammonium cyanide, and leaving a black bulky powder consisting of iron, nickel, and carbon. The original violet compound undergoes the same changes over sulphuric acid as when exposed to the air. Heated in a current of dry ammonia gas to a temperature not above 100°, it is converted into a blue compound, $Ni^2FeCy^6.8NH^3 + 4H^2O$. The crystalline salt deposited from ammoniacal cobalt solutions on addition of potassium ferrocyanide undergoes similar changes when exposed to the air or left over sulphuric acid (Gintl).

Potassium Ferrocyanide in neutral solution is oxidised by hydrogen dioxide to ferricyanide, with formation of potassium hydrate:

$$2K^4FeCy^6 + H^2O^2 = K^6Fe^2Cy^{12} + 2KHO.$$

On the other hand, potassium ferricyanide is reduced by hydrogen dioxide to ferrocyanide and hydroferrocyanide:

$$K^6Fe^2Cy^{12} + H^2O^2 = H^2K^2FeCy^6 + K^4FeCy^6 + O^2;$$

and on this reaction depends the blueing of a mixture of potassium ferricyanide and ferric chloride by hydrogen dioxide (Weltzien, *Ann. Ch. Pharm.* cxxxviii. 129).

Trisodio-potassic ferrocyanide, $KNa^3FeCy^6 + 9H^2O$, is obtained, according to Reindel (*Zeitschr. f. Chem.* [2] iv. 601), by the action of sodium hydrate on potassium ferrocyanide, or by treating sodium ferricyanide with potash and milk-sugar or alcohol. It forms large, shining, light yellow crystals which give off 44 p. c. water at 10°. On exposure to the air it slowly effloresces; over sulphuric acid it quickly gives off the whole of its water. According to Wyrouboff (*ibid.* p. 663), it contains 12 mol. water, like sodium ferrocyanide, $Na^4FeCy^6 + 12H^2O$, with which it is isomorphous.

Rubidium Ferrocyanide (v. 129).

Thallium Ferrocyanide (v. 748).

Yttrium Ferrocyanide, Y^2FeCy^6, crystallises by slow evaporation of the solution obtained by boiling yttria with Prussian blue, in well-developed non-efflorescent crystals: it dissolves in water with yellow colour; is insoluble in alcohol. Potassium ferrocyanide forms in solutions of yttrium salts a granulo-crystalline precipitate, which when dried is a heavy, white, soluble powder probably consisting of $(Y''K^2)FeCy^6$ (Popp, *Ann. Ch. Pharm.* cxxxi. 179).

it dissolves in ammonia, forming palladammonium cyanide, $(N^2H^6Pd^{\prime\prime})Cy^2$, and in potassium cyanide, forming a double salt; its solution in hydrocyanic acid leaves the unaltered cyanide on evaporation.

Potassio-palladious cyanide, $2KCy.PdCy^2$, crystallises with $3H^2O$ in colourless monoclinic prisms, or step-like aggregates of pyramidal forms, which give off 2 mol. water on exposure to the air. The *sodium salt*, $2NaCy.PdCy^2 + 3H^2O$, separates from the solution of palladium cyanide in prussic acid and caustic soda, in crystals isomorphous with those of the potassium salt; the two salts crystallise together from a mixed solution in slightly efflorescent needles. The *barium salt*, $BaCy^2.PdCy^2 + 4H^2O$, obtained by decomposing the corresponding copper salt with baryta-water, forms large monoclinic crystals. The *calcium salt* $CaCy^2.PdCy^2 + 4H^2O$, and the *magnesium salt*, also with 4 mol. water, are prepared like the sodium salt, and crystallise in needles.

The double palladious and platinous cyanides are isomorphous and crystallise together from solution. A *magnesium salt*, $MgPdCy^4.MgPtCy^4 + 14H^2O$, crystallises with difficulty in very soluble tufts of orange-red needles, which become emerald-green at 100°, then colourless, and at 200° give off all their water and turn lemon-yellow. On moistening or breathing upon them, the same series of colours is produced in the reverse order; the solution is quite colourless.

PLATINUM CYANIDES.—A perfectly neutral solution of platinous chloride forms with mercuric cyanide a yellowish-white flocculent precipitate of platinous cyanide, $PtCy^2$, which dissolves in hydrocyanic acid, and is precipitated therefrom only after long boiling. This reaction does not interfere with the separation of palladium and platinum by mercuric cyanide, because the platinum in the solutions is always present, not as platinous, but as platinic chloride, which is not affected by mercuric cyanide. The precipitability of platinous chloride by this reagent affords the means of preparing all the platinous double cyanides directly and free from admixture, namely by precipitating an exactly neutralised solution of platinous chloride with mercuric cyanide, and treating the precipitate with hydrocyanic acid, with addition of the base to be introduced (Rössler, *loc. cit.*).

Ditscheiner (*Wien. Akad. Ber.* i. [2] 373; *Jahresb.* 1865, p. 293) has described the crystalline forms of certain platinocyanides prepared by Schrötter. The *rubidium salt* forms greenish-yellow, slightly fluorescent, monoclinic prisms; the *rubidio-baric salt*, yellowish-white monoclinic prisms; the *ammonium-magnesium salt* $(NH^4)^2PtCy^4.MgPtCy^4 + 6H^2O$, cherry-red, strongly fluorescent crystals belonging to the rhombic system.

Potassio-platinous cyanide, $K^2Pt^{\prime\prime}Cy^4$, takes up iodine with great facility, forming *potassio-platinic iodocyanide*, $K^2Pt^{iv}I^2Cy^4$ or $2KI.PtCy^4$, which separates in large brown shining crystals. When treated with chlorine and bromine, it gives up iodine, and is converted into the corresponding chloro- or bromo-cyanide. Similar salts of other electro-positive metals are easily obtained. $BaBr^2.PtCy^4$ crystallises in large, apparently quadratic tables; the *zinc salt* in cubes; the *copper salt* $CuCl^2.PtCy^4$ in small quadratic pyramids. The *hydrogen salt* $2HBr.PtCy^4$ is very soluble and crystallises in needles. Chlorine acts on bario-platinous cyanide, $BaPtCy^4$, in the same manner as the corresponding potassium salt (ii. 265), converting it into the platinic cyanide $BaPtCy^6$. Bromine acts upon the potassium salt, not on the barium salt; the zinc salt takes up chlorine without perceptible decomposition; but if the potassium salt be first made to unite with iodine, this element may afterwards be replaced by chlorine without further decomposition. When bario-platinous cyanide is heated with water or boiled with excess of silver nitrate, the chlorine is simply removed and not replaced; the chlorine may also be removed by reducing agents (Blomstrand, *Zeitschr. f. Chem.* [2] v. 439).

SILVER CYANIDE.—By heating this compound with ammonia, or any metallic cyanide with an ammoniacal solution of silver, *argentammonium cyanide*, NH^3AgCy, is obtained in large monoclinic crystals, very much like those of selenite. In contact with water they decompose with a hissing noise, and give up all their ammonia (Weith, *ibid.* 380).

THALLIUM CYANIDES (v. 748).—*Thallio-platinous Cyanide*, $2TlCy.PtCy^2$, is obtained by spontaneous evaporation of a solution of thallium carbonate in hydroplatinous cyanide, in blood-red needles with metallic-green surface iridescence (Carstanjen, *Jahresb.* 1867, p. 281).

Detection and Estimation of Cyanogen in Cyanides.—Fröhde (*Pogg. Ann.* cxix. 317) recommends for the detection of cyanogen in solid compounds, the conversion of the latter into sulphocyanates, by fusion with sodium hyposulphite. A small quantity of the anhydrous hyposulphite is fused in a test-tube or in the loop of a platinum wire, with a trace of the substance to be tested, till sulphur begins to volatilise, and the fused mass is dipped into a few drops of ferric chloride solution, whereupon, if cyanogen is present, the well-known blood-red colour is produced.

To apply this method to the quantitative analysis of double cyanides, the compound, carefully mixed with 4 or 5 pts. of barium hyposulphite, is heated in a covered porcelain crucible till the vapours begin to burn on lifting up the lid, and the mass is treated with water. The residual metallic sulphides are dissolved in hydrochloric or nitromuriatic acid; the metals are determined by the usual methods; the filtrate, freed from baryta by a few drops of ammonium sulphate, is supersaturated with hydrochloric acid and evaporated; and the residue is ignited with sal-ammoniac to convert the sulphate into chloride (Fröhde, *Zeitschr. anal. Chem.* iii. 181).

To detect cyanogen in presence of chlorine, the solution may be precipitated with silver nitrate and the precipitate digested with aqueous potash. If a cyanide is present, the diluted filtrate yields a precipitate when supersaturated with nitric acid (Barff, *Laboratory*, p. 345).

CYANINE. See Chinoline-blue (p. 431).

CYANOGEN. The molecule of free cyanogen is represented by the formula

$$\begin{array}{l}C\equiv N\\ |\\ C\equiv N\end{array}$$

On the formation of cyanogen see Cyanides (p. 531). Fröhde is of opinion that the deleterious action of the fumes of burning carbon may be due, not only to the oxides of carbon, but likewise to cyanogen produced in the combustion; in the imperfect combustion of coal he has detected cyanogen by the smell (*Zeitschr. f. Chem.* [2] ii. 540).

Troost a. Hautefeuille (*Compt. rend.* lxvi. 735, 795; *Zeitschr. f. Chem.* [2] iv. 420) have studied the formation of cyanogen and paracyanogen by the decomposition of the cyanides of mercury and silver, and have obtained results differing in several particulars from those of Thaulow (iv. 342). When mercuric cyanide is decomposed in sealed tubes at different temperatures, the relative quantities of cyanogen and paracyanogen produced vary according to the temperature and pressure, the largest proportion of paracyanogen being formed at a comparatively low temperature (350°) and under high pressure. Silver cyanide begins to decompose at a little above 350°. When slowly heated to 440°, and kept at that temperature for some time, it decomposes without fusion or incandescence. If the decomposition be performed in a vacuum, 17 p. c. of the cyanogen evolved is converted into paracyanogen; under ordinary atmospheric pressure, 20 p. c.; and in sealed tubes under a pressure of 60 atmospheres, 64 p. c. If the silver cyanide be slowly heated to 600° under the ordinary pressure, it likewise decomposes without fusion or incandescence, but both these effects are produced when it is very quickly heated. In both cases, however, more than half the cyanogen is evolved as gas, the quantity of paracyanogen formed never exceeding 41 p. c. When the cyanide is heated to the same temperature in sealed tubes, the pressure then amounting to about 80 atmospheres, 76 p. c. paracyanogen is obtained. The paracyanogen is merely mixed, not combined, with the reduced silver, for the latter may be easily extracted by trituration with mercury. The cyanogen gas obtained from silver cyanide has exactly the same properties as that from mercuric cyanide.

The best way of preparing paracyanogen is to heat mercuric cyanide in portions of 5 grms. in sealed tubes to 440° (in boiling sulphur) for 24 hours. About 40 p. c. of the cyanogen is then converted into paracyanogen, which at that temperature remains quite unaltered. It may be freed from mercury by heating it to 440° in a stream of cyanogen gas.

Paracyanogen heated to 860° is completely converted into gaseous cyanogen, which condenses to a liquid in the colder parts of the sealed apparatus. When heated in a vacuum to only 440°, it gives off gaseous cyanogen condensed in its pores, but the actual conversion of the paracyanogen into cyanogen does not begin till it is heated to about 500°; above 550°, a perceptible though very slow decomposition into carbon and nitrogen takes place. Experiments made between 502° and 640° showed that paracyanogen, within certain limits of temperature, is partially converted into cyanogen, and that this conversion attains its limit as soon as the cyanogen exerts upon the paracyanogen a pressure determinate for each temperature. The conversion of paracyanogen into cyanogen takes place very quickly, but that of cyanogen into paracyanogen is very slow. The most favourable temperature for the conversion of cyanogen into paracyanogen is about 500°; but it takes place at 440°, or even at 350°, though very slowly.

Reactions of Cyanogen.—1. When cyanogen gas is passed into strong aqueous *hydrochloric acid*, the liquid after some hours deposits crystals of oxamide, $C^2N^2H^4O^2$, while a small quantity of ammonium oxalate remains in the liquid. Strong aqueous *hydriodic acid* treated with cyanogen also very quickly yields oxamide, iodine being likewise separated, while hydrocyanic acid and ammonium iodide remain in solution (Schmitt a. Glutz, *Zeitschr. f. Chem.* [2] iv. 480). According to Berthelot (*Jahresb.* 1867, p. 347), cyanogen and aqueous hydriodic acid yield as chief products ammonia and ethane:

$$C^2N^2 + 6H^2 = 2NH^3 + C^2H^6,$$

together with oxalic acid and its products of decomposition. When a mixture of cyanogen gas with 12 vol. hydrogen iodide is heated for an hour to dull redness, the cyanogen is resolved into nitrogen and carbon, which latter is deposited in graphitic scales.

Nascent hydrogen, evolved from hydrochloric acid and tin, converts cyanogen into ethylene-diamine, $C^2N^2 + H^8 = N^2(C^2H^4)''H^4$ (Fairley, *Chem. Soc. J.* [2] ii. 362).

CYANOGEN BROMIDE. CNBr.—This compound may be prepared in the same manner as the solid chloride (*infra*) by passing bromine-vapour into a mixture of 1 pt. hydrogen cyanide and 4 pts. anhydrous ether (Gautier). The crystals CNBr, heated in a sealed tube to 130°–140° for six or eight hours, are converted, with partial decomposition, into an amorphous mass coloured yellowish by free bromine. The same product is more easily obtained, and as a perfectly white mass, by heating the crystallised bromide with anhydrous ether. It is a polymeric modification, most probably $C^3N^3Br^3$, insoluble in benzol and absolute alcohol, nearly insoluble in anhydrous ether, melting at a temperature above 300°, and boiling at a still higher temperature, but apparently not volatilising without decomposition. When exposed to moist air or heated with water to 100° in a sealed tube, it is converted into cyanuric acid (Eghis, *Zeitschr. f. Chem.* [2] v. 376).

The great diversities of melting point (4° to 40°) assigned by different chemists to ordinary cyanogen bromide (ii. 277) may perhaps be attributed to admixture of this polymeric modification.

CYANOGEN CHLORIDE. The *liquid chloride* has, according to Salet (*Bull. Soc. Chim.* [2] iv. 105), the vapour-density 2·13, whence its molecular formula is CNCl (calc. 2·129): it follows therefore that the gaseous chloride is merely the vapour of the liquid chloride. Gautier (*ibid.* v. 403) prepares the liquid chloride by rapidly passing chlorine into a mixture of 1 pt. hydrogen cyanide and 4 pts. water, contained in a retort connected with an inverted condenser. If the stream of chlorine be interrupted as soon as the liquid turns green, the formation of the intermediate compound, 2CyCl.CyH, is prevented, and the whole of the hydrocyanic acid is converted into the oily chloride. The product is purified by distillation over mercuric oxide as in Wurtz's method (ii. 280).

According to Regnault, liquid cyanogen chloride boils at 12·66°, under a pressure of 760 mm. and solidifies at about −7° (*Jahresb.* 1863, pp. 70, 74).

To prepare *solid cyanogen chloride*, $C^3N^3Cl^3$, Gautier passes a slow stream of chlorine into a mixture of 1 pt. hydrogen cyanide and 4 pts. anhydrous ether. Viscid drops are then formed, which soon solidify, even if there is no excess of chlorine present. After 24 hours' rest, there is obtained an aggregate of well-defined, apparently monoclinic crystals, having the consistence of wax. If the solution of the hydrogen cyanide is too concentrated, or the stream of chlorine too rapid, or if the liquid be heated, the product obtained after evaporating the ether is a pasty deliquescent mass, which gives off hydrochloric acid on exposure to the air. Solid cyanogen chloride melts at 140° and solidifies again at 130°.

CYANOGEN SELENIDE, $(CN)^2Se$, is formed on introducing dry silver cyanide into a solution of selenium bromide in carbon bisulphide. It is sparingly soluble in that liquid, and crystallises therefrom in colourless or light yellow laminæ having a satiny lustre. When exposed to moist air, they turn red from separation of selenium. Boiling water decomposes the compound immediately into selenium, selenious acid, and hydrocyanic acid; fused with potash it gives off ammonia and leaves a red residue of potassium selenide (R. Schneider, *Pogg. Ann.* cxxix. 364).

CYANOGEN SULPHIDE, $(CN)^2S$, is formed in like manner (together with an easily decomposible compound) by adding 2 pts. silver cyanide to 1 pt. sulphur chloride mixed with 10 to 12 pts. carbon bisulphide, and separates from the heated and filtered liquid in colourless laminæ having a pungent odour. It decomposes spontaneously, losing its penetrating odour, and yielding a yellow substance, probably pseudosulphocyanogen (Schneider, *loc. cit.*; also *Zeitschr. f. Chem.* [2] iv. 504).

CYANURIC ACID. $C^3N^3H^3O^3$.—Formation from cyamelide (p. 517). The crystals of anhydrous cyanuric acid thus obtained are quadratic octohedrons (Voit, *Jahresb.* 1864, 305); those of the hydrated acid are monoclinic (ii. 289).

CYANURIC ETHERS. The cyanuric ethers described in vol. ii. pp. 292–294 are properly carbo-triamides, *e.g.* $N^3\left\{\begin{matrix}(\overset{\prime\prime}{C}O)^3\\(C^2H^5)^3\end{matrix}\right.$, and are resolved by boiling with alkalis into carbonic acid and the corresponding monamines. The true cyanuric ethers or alcoholic cyanurates, $C^3\left\{\begin{matrix}N^3\\(OR)^3\end{matrix}\right.$, have recently been discovered by Hofmann (*Deut. Chem. Ges. Ber.* 1870, 269; *Zeitschr. f. Chem.* [2] vi. 492). They are formed, together with the alcoholic cyanates (p. 519), when gaseous cyanogen chloride is passed into a solution of sodium methylate, ethylate, &c., in the corresponding alcohol, and are resolved by boiling with alkalis into cyanuric acid and in alcohol; *e.g.* $(CN)^3(OCH^3)^3 + 3H^2O = (CN)^3(OH)^3 + 3CH^3OH$. Phenyl cyanurate, $(CN)^3(OC^6H^5)^3$, is obtained by the action of cyanogen chloride on sodium phenate dissolved in absolute alcohol. All these ethers are crystalline. The formation of the methylic and ethylic cyanurates is accompanied by that of ethers of amido- and diamido-cyanuric acid.

CYAPHENINE. nC^7H^5N. *Kyaphenine* (iii. 449).—This compound, which Cloez obtained by heating potassium cyanate with benzoyl chloride, is also produced by heating benzonitrile bromide, C^7H^4NBr (or the precipitate thrown down by water from the alcoholic solution of the crude product obtained by the action of bromine on benzonitrile), with lime; also by heating this bromide by itself to 150°–160°: consequently it is always found amongst the products of the action of bromine on benzonitrile (Engler, *Ann. Ch. Pharm.* cxxxiii. 137).

Cloez assigned to cyaphenine the formula $C^{21}H^{15}N^3$, regarding it as an analogue of cyanethine, $C^9H^{15}N^3$; but according to Engler (*ibid.* cxlix. 310), this supposed analogy does not rest on any satisfactory foundation. Cyaphenine does not appear to form salts with acids; it does not give off ammonia when boiled with alcoholic potash, and only traces when heated therewith in sealed tubes to 150° [the ammonia which Cloez obtained was perhaps derived from the decomposition of admixed benzonitrile]; and when heated with a large excess of fuming hydriodic acid in sealed tubes to 220°, it yields only benzoic acid (not a polymeride thereof) and a very small quantity of an oil, probably hexane.

CYMENE. $C^{10}H^{14}$.—See BENZENE, HOMOLOGUES OF (p. 302).

CYMIDINE. This base, discovered by Barlow and obtained by reduction of nitrocymene, is isomeric (not identical, as stated in vol. ii. p. 297) with monocymylamine, which is produced, together with di- and tri-cymylamine, by the action of ammonia on cymyl chloride. Regarding cymene as methyl-propyl-benzene, $C^6H^4\left\{\begin{matrix}CH^3\\C^3H^7\end{matrix}\right.$, the difference of structure between the two isomeric bases may be represented by the following formulæ:

$$\underset{\text{Cymidine.}}{C^6H^3(NH^2)\left\{\begin{matrix}CH^3\\C^3H^7\end{matrix}\right.}\qquad\qquad\underset{\text{Cymylamine.}}{C^6H^4\left\{\begin{matrix}CH^2(NH^2)\\C^3H^7\end{matrix}\right.}$$

CYRTOLITE. A zirconium silicate found in the granite of Rockport, Massachusetts, in brown-red crystals similar to those of the zircon of Expailly, but having their end-faces curved (hence its name). Sp. gr. 3·895 to 4·04 (Cooke); 3·850 to 3·970 (Knowlton). Hardness, before ignition, 5 to 5·5; after ignition, 7 to 7·5. Gives by analysis, 26·18 to 26·48 silica, 60·00 to 61·33 zirconia, and 4·55 to 4·58 water, together with small quantities of the oxides of the cerium metals, iron, uranium, and tin, and traces of copper, manganese, magnesium, and fluorine (Knowlton, *Sill. Am. J.* [2] xliv. 224; *Jahresb.* 1867, p. 988).

CYTISINE. $C^{20}H^{27}N^3O$ (Husemann a. Marmé, *Zeitschr. f. Chem.* [2] i. 161; Husemann, *ibid.* v. 677).—A poisonous alkaloïd occurring in the ripe seeds of *Cytisus Laburnum*, and other species of the same genus; obtained in an impure state by Chevallier a. Lassaigne (ii. 301). To obtain it, the extract of the seeds prepared with slightly acidulated water, purified by precipitation with basic lead acetate, and evaporated, is mixed with tannic acid; the resulting precipitate, mixed with litharge and dried over the water-bath is treated with alcohol, which dissolves out the cytisine; and the solution evaporated to a syrup is strongly acidulated with nitric acid and mixed with 6 to 8 vol. absolute alcohol. The solution thus obtained, after being decanted from a resinous body which separates on cooling, yields an abundant crystallisation of cytisine nitrate, which, by repeated crystallisation from boiling water, is obtained in large colourless well-defined crystals. This salt dried, pulverised, and mixed with highly concentrated potash-ley, yields cytisine as a clear colourless oily layer which solidifies on cooling. It is then removed, rinsed with a little cold water, again fused with potash, and after separation and rinsing as before, is left for some time in an atmosphere containing carbonic acid, to convert the free potash which adheres to it into carbonate; lastly, it is dissolved in absolute alcohol, and the solution is evaporated to a syrup, whereupon it solidifies on cooling to a dazzling white crystalline mass.

Cytisine is not deliquescent. It has a bitterish caustic taste, melts at 154·5° (corr.), and sublimes when cautiously heated in very thin flexible needles or laminæ. It dissolves in water and alcohol in almost all proportions, but is nearly insoluble in ether, chloroform, benzol, and carbon bisulphide. It is one of the strongest of the vegeto-alkaloids, expelling ammonia from its salts even at ordinary temperatures. It does not reduce cupric oxide.

Cytisine is a polyacid base. The only one of its salts that crystallises well is the *nitrate*, $C^{20}H^{27}N^{3}O.2HNO^{3} + 2H^{2}O$, which separates from water or dilute alcohol in thick transparent prisms. It has a more bitter taste than the free base, dissolves in less than its own weight of boiling water, and crystallises out almost completely on cooling. It is slightly soluble in dilute alcohol, quite insoluble in absolute alcohol and in ether. The sulphate, phosphate, formate, acetate, propionate, butyrate, valerate, oxalate, and tartrate, are all deliquescent and impossible or difficult to crystallise.

The *hydrochloride* is easily soluble in water, less soluble in absolute alcohol. The solution evaporated over the water-bath leaves a salt which, after drying at 120°, contains $C^{20}H^{27}N^{3}O.3HCl$. The *platinochloride*, $C^{20}H^{27}N^{3}O.2HCl.PtCl^{4}$, is precipitated in orange-yellow flocks, gradually changing into an aggregate of microscopic needles. The mother-liquor yields on evaporation light yellow crystalline nodules containing $C^{20}H^{27}N^{3}O.4HCl.PtCl^{4}$. The *aurochloride*, $C^{20}H^{27}N^{3}O.2HCl.2AuCl^{3}$, forms tufts of slender needles. *Mercuric chloride* forms no precipitate in solutions of the hydrochloride; but on adding it to a solution of the free base containing not more than 1 pt. in 1,000, it throws down a white precipitate of the compound $C^{20}H^{27}N^{3}O.2HgCl^{2}$, which gradually changes into hard roundish crystalline masses, easily soluble in hydrochloric and in nitric acids.

Reactions of Cytisine.—*Potassio-cadmic iodide* and *potassio-mercuric iodide* produce, even in very dilute solutions of the nitrate, white flocculent precipitates, afterwards becoming crystalline. A solution of iodine in potassium iodide forms in the weakest solutions, a dark red-brown precipitate, amorphous at first, but converted on standing into beautiful dark red translucent prisms. *Bromine-water* is an equally delicate test, producing a fiery orange-yellow precipitate, and a slight turbidity even in solutions diluted 15,000 times. *Sodium phosphomolybdate* forms in the strongly acidulated solution a yellow precipitate; *tannic acid* forms little or no precipitate in acid solutions, but in a solution neutralised with soda it forms a copious white flocculent precipitate. An alcoholic solution of *picric acid* forms with the free base or the nitrate, a light-yellow precipitate which soon becomes crystalline. Strong *sulphuric acid* dissolves cytisine without colour. On adding to the solution small pieces of *potassium dichromate*, it assumes a pure yellow colour, changing to dirty brown and finally to green; *sodium molybdate* produces no alteration; a drop of *nitric acid* colours the solution orange-yellow after a few minutes.

The unripe seeds and pods of the laburnum contain another basic substance called **laburnine**, likewise poisonous, but less powerfully basic than cytisine. To obtain it, the aqueous extract, purified with basic lead acetate, is precipitated by sodium phosphomolybdate, and the precipitate, after drying with chalk, is boiled with alcohol. The base separated, for further purification, from its platinum salt, forms light crystalline groups of hydrated monoclinic prisms. It is very soluble in water, dissolves with difficulty in alcohol, scarcely at all in ether, and gives off ammonia when treated with potash, even at ordinary temperatures (Husemann a. Marmé, *loc. cit.*).

D

DACITE. Greenstone-trachyte occurring at several localities in Transylvania (*Jahresb.* 1867, p. 1020).

DAMALURIC ACID. $C^6H^{10}O^2$.—An acid of the acrylic series, extracted by Städeler (ii. 301), together with damolic acid, from cows' urine. According to W. Werner (*Zeitschr. f. Chem.* [2] iv. 413), it crystallises in rhomboïdal needles melting at 50°–53°, or by evaporation in a vacuum, in prisms which melt at 39°–40° when recently crystallised, but whose melting point rises to 50° after they have been exposed for some time to the air. This prismatic modification is optically lævogyrate, the ordinary modification dextrogyrate.

Damaluric and damolic acids are obtained in the same preparation as taurylic acid (v. 701). The oily mixture of these acids is agitated with sodium carbonate; the evaporated saline solution, freed from taurylic acid by agitation with ether, is distilled with sulphuric acid; and the distillate is saturated with barium carbonate. The filtered solution deposits, first crystals of barium damolate, then the damalurate—from which the pure acid may be obtained—and lastly salts of fatty acids more or less impure (Städeler).

DAMBONITE. $C^4H^8O^3$ (A. Girard, *Compt. rend.* lxvii. 820).—A crystallised saccharine substance existing in a peculiar kind of caoutchouc exported from the French colony of Gaboon on the west coast of Africa. This caoutchouc, which differs in appearance from other species, is not obtained from trees of the genus Ficus, or from Euphorbiaceæ, but from climbing plants the botanical species of which is unknown. The exuded juice, coagulated by exposure to the air, is kneaded into loaves called by the natives *n'dambo.* These loaves often contain a white liquid which gradually alters, the caoutchouc then losing its valuable properties. A quantity of the caoutchouc thus altered having been heated to convert it into tar, the workmen observed, amongst the condensed volatile products, a white sweet substance crystallised in needles. This substance is dambonite; it exists ready-formed in the Gaboon caoutchouc. The pure recently imported caoutchouc-juice, if evaporated at a gentle heat, dries up to a coloured crystalline mass, from which the pure dambonite is easily extracted by solution in alcohol. The sample examined by Girard yielded 0·5 p. c.

Dambonite is white, easily soluble in water and in alcohol of ordinary strength, sparingly soluble in absolute alcohol. It melts at 190°, and when cautiously heated sublimes at 200°–210°, without decomposition, in long slender shining needles. From alcohol it crystallises in six-sided prisms; from water, with difficulty, in oblique prisms containing $2C^4H^8O^3 . 3H^2O$. Dilute sulphuric acid does not act upon it; the hot strong acid carbonises it; cold nitric acid dissolves it without alteration; hot nitric acid oxidises it to oxalic and formic acids. Concentrated alkalis do not act upon it even at 100°, but they considerably diminish its solubility in water. Lime-water, baryta-water, and lead acetate give no precipitates. It does not reduce alkaline cupric solutions, and is not susceptible either of alcoholic or of lactic fermentation. It unites with *potassium iodide*; a mixture of the warm alcoholic solutions of the two bodies deposits, on cooling, beautiful crystals of the compound $KI . 2C^4H^8O^3$.

DAMBOSE. $C^3H^6O^3$ (Gerard, *loc. cit.*).—Dambonite is decomposed by hydriodic acid, even at ordinary temperatures, and quickly at 100°, by hydrochloric acid also at 110°, yielding methyl iodide or chloride and dambose, a crystallisable sugar isomeric with glucose:

$$C^4H^8O^3 + HI = CH^3I + C^3H^6O^3.$$

To prepare dambose, dambonite is heated to 100° in sealed tubes with excess of fuming hydriodic acid; the solution decanted from the separated methyl iodide is mixed with alcohol of 95 p. c., which precipitates the dambose completely as a white powder; the precipitate is washed with alcohol and dissolved in a small quantity of boiling water; and this solution is mixed with 100 times its volume of boiling alcohol. The dambose is then deposited on cooling in beautiful six-sided prisms. It is easily soluble in water, though less soluble than dambonite, and crystallises from water in rather thick anhydrous prisms, whereby it is distinguished from inosite, which it otherwise resembles. It is very slightly soluble in aqueous alcohol, insoluble in absolute alcohol.

Dambose is a very stable substance, not being decomposed at 230°, at which temperature however it melts and begins to become coloured; at a higher temperature it suffers decomposition. It is not fermentable. *Bromine* does not attack it at 160°, but at 180° hydrobromic acid and a brominated substitution-product are formed. *Phosphorus pentachloride* attacks it at 150°, forming hydrochloric acid and a product smelling like camphor. Fuming *nitric acid* dissolves it without alteration at ordinary temperatures, but boiling nitric acid converts it into oxalic acid.

Dambose triturated with cold strong *sulphuric acid* dissolves to a colourless syrup which, when diluted with water and neutralised with barium or lead carbonate, yields easily soluble gummy salts, which are permanent at 150°, and are precipitated by alcohol from their aqueous solutions. The barium salt contains $C^6H^{16}S^2O^{15}Ba = C^6H^{16}\left\{\begin{array}{c} SO^2 \quad O \\ Ba \\ SO^2 \quad O \end{array}\right\}O^9$; the lead salt, $C^6H^{16}S^2O^{15}Pb$. *Dambosulphuric acid* separated from either of those salts dries up in a vacuum to a thick syrup, which dissolves in water and in alcohol, and decomposes in moist air, with separation of dambose. This acid instantly reduces alkaline cupric solution, a property not exhibited by free dambose.

Concentrated *alkalis* do not act upon dambose at ordinary temperatures, and *metallic salts* do not precipitate its aqueous solution; but on adding an alcoholic solution of ammoniacal lead acetate to an aqueous solution of dambose, a white precipitate soluble in water is produced, which when dried at 120° has the composition $(C^3H^4O)^2Pb.PbO$. In like manner a solution of baryta in wood-spirit forms a white, easily decomposible precipitate, which when dried at 110° appears to have the composition $(C^3H^4O^3)BaO$.

The reactions above described show that dambose is a polyatomic alcohol, and dambonite its methylic ether:

$$(C^3H^3)'''\left\{\begin{array}{l} OH \\ OH \\ OH \end{array}\right. \qquad\qquad (C^3H^3)'''\left\{\begin{array}{l} OH \\ OH \\ OCH^3 \end{array}\right.$$

Dambose. Dambonite.

DANALITE. A mineral resembling rhodonite, occurring in the granite of Rockport, Massachusetts; flesh-coloured to grey, translucent, brittle, with slightly conchoïdal fracture; hardness 5·5 to 6; sp. gr. 3·427. From its internal crystalline structure it appears to consist of holohedral forms of the regular system. Analysis gave 31·73 p. c. SiO^2, 27·40 FeO, 17·51 ZnO, 6·28 MnO, 13·88 GlO and 5·48 S (= 102·28), whence it is inferred to be an isomorphous mixture of a regular silicate with the sulphides of zinc and iron, and perhaps of manganese: $(MO.GlO)SiO^2 + MS$ (J. F. Cooke, jun., *Sill. Am. J.* [2] xlii. 73).

DAPHNIN and **DAPHNETIN** (ii. 303). According to Rochleder (*Wien. Akad. Ber.* xlviii. [2] 236; *Jahresb.* 1863, p. 591), daphnin is isomeric or polymeric with æsculin, and daphnetin dried at 100° with hydrated æsculetin. Daphnetin dried at 220° in a stream of carbon dioxide gives off 1 mol. water, and has then the same composition as æsculetin.

DECYLIC COMPOUNDS. Compounds derived from the fundamental hydrocarbon $C^{10}H^{22}$, decyl hydride or diamyl (p. 105). This hydrocarbon, obtained by Pelouze and Cahours from American petroleum, and by Wurtz by treating diamylene with bromine (ADDENDA, vol. v. p. 1090), is likewise produced by the action of hydriodic acid on coal-tar cymene, $C^{10}H^{14}$; and, together with other hydrocarbons of the same series, by the action of hydriodic acid on naphthalene, $C^{10}H^8$, and acenaphthene, $C^{12}H^{10}$ (Berthelot, *Jahresb.* 1867, pp. 346, 592, 596, 710).

Decylene, $C^{10}H^{20}$, produced by the action of alcoholic potash on decyl chloride, $C^{10}H^{21}Cl$ (v. 1091), unites with bromine, forming $C^{10}H^{20}Br^2$, which when heated till it begins to decompose, and then treated with alcoholic potash, yields a mixture of decylene precipitable by water, and bromodecylene, $C^{10}H^{19}Br$. This last compound, separated by fractional distillation, is a colourless liquid which gradually turns brown, has a sp. gr. of 1·109 at 15°, and boils at about 215°. Heated for six hours to 180° in closed vessels with a saturated alcoholic solution of potash, it yields a mixture of ethyl-decenylic ether, $(C^2H^5)(C^{10}H^{19})O$, and decenylene, $C^{10}H^{18}$, which may be separated by fractional distillation finally over sodium. Decenylene has a faint alliaceous odour, boils at about 165°, and when treated with bromine in a cooled vessel, forms at first the liquid dibromide $C^{10}H^{18}Br^2$, which by several hours' contact with excess of bromine, is converted into a thick oily tetrabromide, $C^{10}H^{16}Br^4$ (Reboul a. Truchot, *Bull. Soc. Chim.* [2] viii. 422).

DEHYDRACETIC ACID. $C^8H^8O^4$ (Geuther, *Jenaische Zeitschr.* ii. 387; iv. 241; *Jahresb.* 1865, p. 303; *Zeitschr. f. Chem.* [2] iv. 655).—An acid said to be produced by the action of hydrochloric or carbonic acid on the sodium salt of ethyl-diacetic acid (Wanklyn's sodium triacetyl, p. 15); also, according to R. Brandes (*Jahresb.* 1866, p. 307), in the rectification of methyldiacetic acid, $C^5H^8O^3$, and by the action of carbon dioxide on sodium methyldiacetate at 170°. To prepare it, the brown substance which remains when sodium ethyldiacetate is heated in a stream of carbon dioxide is dissolved in water; the solution, freed from colouring matter by agitation with ether, is supersaturated with hydrochloric or acetic acid; and the dehydracetic acid thereby separated is purified by recrystallisation from ether, and then from water; it is thus obtained in orthorhombic crystals. It melts at 108·5°–109°, boils at 269·6°, dissolves in about 1,000 pts. water at 6°, more abundantly in boiling water, and in alcohol and ether. It is monobasic; its *sodium salt* $C^8H^7O^4Na + H^2O$ forms long needles soluble in water; the barium salt $(C^8H^7O^4)^2Ba + H^2O$, rhombic tables; the *calcium salt* $(C^8H^7O^4)^2Ca$ (at 150°), thick rhombic prisms. The solution of the barium salt forms crystalline precipitates with silver nitrate, zinc acetate, and cupric acetate, but not with lead acetate.

DELPHININE. This alkaloïd, obtained from the seeds of *Delphinium Staphisagria* (ii. 310), has the composition $C^{24}H^{35}NO^2$; its platinochloride is nearly white, insoluble in water, ether, and alcohol, and contains $2(C^{24}H^{35}NO^2.HCl).PtCl^4$ (J. Erdmann, *Jahresb.* 1864, p. 450).

DELVAUXITE. This mineral from Liège consists, according to Church (*Chem. News*, x. 145), of $2Fe^2O^3.P^2O^5 + 3H^2O$ (at 100°). The air-dried mineral gives off 16·9 p. c. water at a red heat. A specimen from Nenacovic, near Lodenic in Bohemia, analysed by E. Boricky (*Jahresb.* 1867, p. 1001), exhibited the composition $2CaO\ P^2O^5 + 5FeO^3.P^2O^5 + 16H^2O$, assigned to the mineral by v. Hauer (ii. 310).

DEOXYBENZOÏN. $C^{14}H^{12}O$.—See Benzoïn (p. 332).

DESOXYANISOÏN. $C^{16}H^{16}O^3$.—A crystalline substance produced by the action of dilute sulphuric acid on hydranisoïn or isohydranisoïn. It is very soluble in alcohol and ether, and melts at 95° (A. Rossel, *Zeitschr. f. Chem.* [2] v. 562). See Anisoïn (p. 175).

DEVILLIN. A calcio-cupric sulphate found, together with langite, in Cornwall. (See Sulphates.)

DEXTRIN. Limpricht (*Jahresb.* 1865, p. 673) has obtained this substance from the flesh-juice of the horse. The liquid freed from albumin and from substances precipitable by baryta-water, yielded on careful evaporation, first crystals of creatine, then a gelatinous mass, from which, by repeated solution in water and precipitation with alcohol, dextrin was obtained, exhibiting all the properties of that prepared from starch. 200 lb. of the flesh of a young horse yielded about 400 grams of dextrin.

Dextrin dissolves in acetic anhydride at 150°, forming triacetyl-dextrin, $C^6H^7(C^2H^3O)^3O^5$. The same compound is formed by the action of acetic anhydride upon starch at 160°. It is insoluble in water, but dissolves in glacial acetic acid, and is precipitated therefrom by water in white amorphous flocks. By caustic alkalis it is easily resolved into acetic acid and dextrin (Schützenberger a. Naudin, *Compt. rend.* lxviii. 814; *Zeitschr. f. Chem.* [2] v. 264).

DIACETAMIDE. Formation from acetonitrile (p. 524).

DIALLYL. See Allyl.

DIALOSE. A substance somewhat resembling disintegrated cellulose, obtained from the pericarp of a Chinese leguminous plant (a species of *Dialium*). It swells up in water to a bulky colourless jelly, the gummy solution of which is not precipitated by baryta-water, basic-lead acetate, or alcohol. The desiccated amorphous substance dissolves in strong sulphuric acid, but does not thereby acquire the property of becoming coloured by iodine (Payen, *J. Pharm.* [4] iv. 339).

DIALURIC ACID. $C^4H^4N^2O^4$.—This acid may be regarded as derived from alloxan, $C^4H^2N^2O^4$, by fixation of 2 at. hydrogen, or from barbituric acid, $C^4H^4N^2O^3$, by fixation of 1 at. oxygen (v. 961). It may also be regarded as *tartronyl-urea*,

$$N^2\left\{\begin{matrix}(CO)'' \\ (C^3H^2O^3)''. \\ H^2\end{matrix}\right.$$

To prepare dialuric acid from uric acid, Baeyer (*Ann. Ch. Pharm.* cxxvii. 1) converts the latter into alloxan by Schlieper's method (treatment with hydrochloric acid and potassium chlorate), and mixes the hot solution of the alloxan (decolorised, if necessary, by animal charcoal) at once with a solution of tin in hydrochloric acid containing a quantity of tin equal to that of the uric acid employed. A quantity of hydrochloric acid is then added sufficient to make up the volume of the mixture to 4 litres for each pound of uric acid used. The liquid, after standing for a day, deposits dialuric acid (about 50 p. c. of the uric acid) in stellate groups of short four-sided prisms, having a faint yellowish colour. The mother-liquor does not yield any further quantity. To prepare dialuric acid from alloxantin, sodium-amalgam is added to a thick pulp of the latter, with constant stirring, as long as any action takes place, and the sodium dialurate, formed according to the equation,

$$C^8H^4N^4O^7 + 2H^2O + Na^2 = H^2O + 2C^4H^3NaN^2O^4,$$

is decomposed with hydrochloric acid.

Dialuric acid heated with acetic acid and an alkaline nitrite is converted into allantoïn, without the formation of any other organic compound; probably thus:

$$\underset{\text{Dialuric acid.}}{2C^4H^4N^2O^4} + \underset{\text{Nitrous acid.}}{4NO^2H} = \underset{\text{Allantoïn.}}{C^4H^6N^4O^3} + 4CO^2 + 3H^2O + N^2O^2 + N^2$$

(W. Gibbs, *Zeitschr. f. Chem.* v. 604).

DIAMOXALIC ACID. See Oxalic Ethers (iv. 276).

DIAMYL and **DIAMYLENE.** See Amyl and Amylene (pp. 105 and 122).

DIAMYL-ACETONE. See Ketones.

DIARBUTIN. See Arbutin (p. 192).

DIAZO-COMPOUNDS. See Aromatic Series (p. 207).

DIBARBITURIC ACID. See Uric Acid, Derivatives of (v. 962).

DIBENZYL. See Benzyl (p. 334).

DICYANIC ACID, $C^2N^2H^2O^2$, is produced, according to Pönsgen (*Ann. Ch. Pharm.* cxxviii. 339; *Jahresb.* 1863, 353), by the action of nitrous acid on cyanurea (cyano-carbamide) suspended in water:

$$CH^3(CN)N^2O + NHO^2 = C^2N^2H^2O^2 + H^2O + N^2.$$

It crystallises from hot water in efflorescent monoclinic prisms containing 3 mol. water. It is bibasic, forming acid and neutral salts, *e.g.* $C^2N^2HAgO^2$ and $C^2N^2Ag^2O^2$. According to Hallwacks, however (*Zeitschr. f. Chem.* [2] vi. 353), Pönsgen's cyanurea is nothing but impure ammelide, and his dicyanic acid is most probably identical with cyanuric acid.

Hofmann has lately shown that the crystalline body produced on bringing phenyl cyanate in contact with triethylphosphine, which he formerly regarded as phenyl cyanurate (iv. 611), is in reality diphenyl-isodicyanate or diphenyl dicarbodiamide, $N^2(CO)^2(C^6H^5)^2$ (*Deut. Chem. Ges. Ber.* 1871, 246).

DICYANODIAMIDE. See Cyanamide (p. 517).

DIDYMIUM. Di. *Atomic Weight* 96.—Bunsen (*Pogg. Ann.* cxxviii. 100) has made a very exact examination of the absorption-spectrum of didymium salts. As the breadth of the dark bands varies with the thickness and concentration of the absorbing solution, it is necessary to ensure that the light, in its passage through the liquid, is always exposed to the action of the same quantity of the absorbing substance. If then l and l' denote the thickness of two transparent layers of didymium salt, solid or liquid, and d, d' the quantities of didymium contained in a unit of volume of these layers, the condition just mentioned will be satisfied if $ld = l'd'$, that is to say, if the thicknesses of the two layers are inversely proportional to the quantities of didymium contained in them. By examining the spectra of various didymium salts in ordinary and in polarised light, with a very powerful spectral apparatus (four flint-glass prisms of 60°, and three of 45°) and a magnifying power of 40°, Bunsen finds that the dark bands vary in breadth, and to a certain extent also in position, accordingly as the ordinary or the extraordinary ray is used; with unpolarised light intermediate results are obtained. Moreover, the positions of minimum illumination vary according to the nature of the salts: in didymium chloride (molec. wt. 167), didymium sulphate (mol. wt. 92), and didymium acetate (mol. wt. 214), the bands are shifted towards the red end of the spectrum in the order of the molecular weights of the respective salts. The positions of the principal absorption-bands on Bunsen's scale (SPECTRAL ANALYSIS, vol. v. p. 382) are as follows:

α 49–56; β 71–75; δ 27–31; γ 91–93; $\beta' = 76–80$.

The others occupy the divisions 21–23, 30-31, 41–42, 68–69, 96, 98–101, 114–119. The bands α, β, β', γ, remain the longest, as the solution is more and more diluted. α and β are the bands discovered by Gladstone (ii. 322).

Bunsen has also devised the following method of converting the dark bands of the absorption-spectrum into bright ones: A small quantity of didymium oxide is fused with phosphorus salt in a loop of platinum wire so as to obtain an amethyst-coloured bead free from bubbles, and this bead is placed before the slit of the spectroscope, between an incandescent capillary platinum wire serving as the source of light, and a small convex lens of short focus, so adjusted as to throw the image of the bead upon the slit. The stronger absorption-bands will then be distinctly seen, especially Di α. If the bead be then gradually heated by a non-luminous flame placed below it, the band Di α will increase in breadth and intensity, so long as the bead does not become red-hot; but as soon as the temperature of bright redness is attained, this band disappears completely; and if the incandescent platinum wire which serves as the source of light be gradually moved farther off, the dark band α will be replaced by a similar but luminous band upon a dark ground. Indications of a similar inversion are likewise exhibited by the other absorption-bands (*Ann. Ch. Pharm.* cxxxi. 255).

Quantitative Estimation.—The quantity of didymium contained in a mixture may be approximately estimated by the spectral method, viz. by dissolving a decigram of the substance under examination in an acid, placing the solution in a calibrated test-tube before the slit of a spectroscope, and ascertaining the degree to which it must be diluted in order that it may exhibit an absorption-spectrum equal in intensity to that produced by a solution containing a decigram of pure didymium oxide in every 10 cubic centimetres, placed in a tube of the same diameter and examined by the same spectroscope. The quantity of didymium in the original solution may then be calculated by a proportion, inasmuch as the quantity of water added to it will be greater or less in proportion to the quantity of didymium present (Bahr a. Bunsen, *Ann. Ch. Pharm.* cxxxvii. 1).

Separation from Lanthanum.—No exact method of separating didymium from lanthanum has yet been discovered, but the following approximate method is given by Damour and Deville (*Bull. Soc. Chim.* [2] ii. 339). The solution of the mixed nitrates is evaporated to dryness in a shallow platinum capsule; and the residue, after being heated for a few minutes to 400°–500°, is treated with water, which dissolves chiefly the lanthanum salt, leaving undissolved a flocculent powder consisting of basic didymium nitrate, $3DiO.Di(NO^3)^2.5H^2O$. This is separated by filtration, and the evaporated solution is treated three times in the same manner till nothing but colourless lanthanum nitrate passes into solution. The separated nitrates are then strongly ignited and the residual oxides weighed. The quantity of didymium oxide thus ascertained may be 5 or 6 p. c. too high; that of the lanthanum oxide proportionally too low.

DIETHOXALIC ACID. See OXALIC ETHERS (iv. 273).

DIETHYL. See ETHYL.

DIETHYLACETONE. See KETONES.

DIFRANGULIC ACID. See FRANGULIC ACID.

DIGITALIN. According to Lefort (*J. Pharm.* [5] vi. 424), the diversities in the properties and reactions of digitalin, as described by different observers, are due to the existence of two modifications of this body. The more soluble (so-called German) digitalin is obtained from the seeds, the less soluble or crystallised variety from the leaves of the foxglove, in which this latter modification predominate. To prepare ordinary (crystallised) digitalin, Lefort exhausts the leaves at 40°–50° with a mixture of equal parts of water and alcohol; precipitates the extract with a slight excess of basic lead acetate; removes the excess of lead from the filtrate with sodium carbonate; and mixes the concentrated filtrate with tannic acid. The precipitated brown digitalin tannate is washed with lukewarm water, digested with finely pulverised lead oxide, and then treated with alcohol. The solution, after declorisation with animal charcoal, yields on evaporation crystallised digitalin, while the more soluble modification remains in the mother-liquor.

Nativelle (*J. Pharm.* [4] ix. 255) prepares crystallised digitalin by mixing 100 pts of pulverised digitalis with a solution of 25 pts. neutral lead acetate in 100 pts. water, leaving the whole to itself for 12 hours, and then exhausting with water. The residue is exhausted with alcohol of 50 p. c.; the solution is mixed with 4 pts. neutral lead acetate, filtered, decolorised with animal charcoal, again filtered, and mixed with a solution of 2 pts. sodium phosphate; and the liquid filtered from the resulting precipitate is freed from alcohol by distillation in the water-bath. The residue of the distillation contains crystals in suspension surrounded by a yellow very bitter substance. The whole is evaporated over the water-bath to about 10 pts.; and the precipitate is washed on a filter with cold water, pressed between paper, dissolved in twice its weight of warm alcohol at 60°, and left to stand in a cool place. The liquid then deposits crystals of an inactive substance, and afterwards yellowish radiate crystals of digitalin. These are recrystallised from alcohol of 80 p. c., with addition of animal charcoal, and the dried and pulverised crystals are drenched and strongly agitated with 20 pts. of pure chloroform, which dissolves only the digitalin, leaving the inactive substance behind. On distilling off the chloroform, colourless digitalin remains behind, which may be purified by repeated crystallisation from alcohol and boiling with animal charcoal.

Crystallised digitalin is neutral, inodorous, and has a very bitter persistent taste; soluble in chloroform in all proportions, in about 10 pts. alcohol of 90 p. c. at ordinary temperatures, more easily at the boiling heat, less easily in absolute alcohol, nearly insoluble in pure ether, and in water even at the boiling heat. Sulphuric acid dissolves it with green colour, changed to red by bromine-vapour, but becoming green again on addition of water. Hydrochloric acid dissolves it with greenish-yellow colour, and from this solution water precipitates it in the form of a resin. The analysis of pure digitalin leads to the formula $C^{25}H^{40}O^{15}$.

The crystalline substance insoluble in chloroform, originally mixed with the digitalin, is easily purified by recrystallisation from alcohol. It crystallises in slender colourless needles which are perfectly tasteless, neutral, and free from nitrogen. It is less soluble in alcohol than digitalin, nearly insoluble in ether, chloroform, and water. Sulphuric acid dissolves it with currant-red colour, changing to yellow on addition of water. It dissolves without colour in nitric acid, incompletely in hydrochloric acid. Its composition has not been ascertained (Nativelle).

DIGLYCERIN. See Glyceryl Hydrates (ii. 894).

DIGLYCOL-ETHYLENIC ACID. See Glycollic Acid (ii. 914; also in this volume).

DIGLYCOLLAMIC ACID. See Glycollamic Acid.

DIGLYCOLLIC ACID. See Glycollic Acid.

DIGLYCOLLIMIDE. See Glycollic Acid, Amides of.

DILACTIC ACID. See Lactic Acid (iii. 461).

DILITURIC ACID. See Appendix to vol. ii. p. 965.

DIMETHOXALIC ACID. See Oxalic Ethers (iv. 274).

DIMETHYL. See Methyl.

DIMETHYLACETONE. See Ketones.

DIOXINDOL. See Indol.

DIPHENOL. See Phenol.

DIPHENYL. See Phenyl.

DIPTYL. This name is applied by Perkin to a radicle, C^7H^3O, belonging to the cinnamyl series, supposed to exist in coumarin, that substance having the composition of acetyl-diptyl, $C^2H^3O.C^7H^3O$ (p. 498).

DISPOLINE. $C^{11}H^{11}N$ (C. Gr. Williams, *Laboratory*, p. 109).—A base homologous with chinoline, obtained, together with many others, in the distillation of cinchonine with potash, and occurring in that portion of the crude distillate which boils between 282° and 304°. The solution of this distillate in hydrochloric acid is warmed with a little nitric acid, to decompose pyrrol and other impurities, and the solution filtered from the separated resinous mass is precipitated with platinum chloride, which throws down in the first instance the platinochlorides of bases of higher molecular weight. The liquid filtered from this precipitate yields with platinic chloride an orange-coloured granular powder not fusible at 100°. On distilling this precipitate, neutralising the distillate with hydrochloric acid, and again precipitating with platinic chloride, a platinochloride is obtained having the same composition as the preceding, viz. $2(C^{11}H^{11}N.HCl).PtCl^4$.

DISSOCIATION. See Chemical Action (pp. 424–429).

DISTYROL. $C^{16}H^{16}$.—See Cinnamene (p. 466).

DITOLYL. See Tolyl.

DIXYLYL. See Xylyl.

DRACYLIC COMPOUNDS. See Benzoic Acid, Derivatives of (pp. 310, 313, 314, 316, 320, 321).

DRAGON'S BLOOD. See Resins.

DRAGON'S BLOOD TREE. *Croton Erythræma.*—The juice of this tree (indigenous in Brazil) contains—besides tannin, gallic acid, mucus, pectin, albumin, sugar, colouring matter, resin, and mineral salts—an acid, called erythraemic acid, allied to tannic acid. This acid separates, on mixing the fresh juice with water, as a tasteless and scentless brick-red powder, insoluble in cold water and in ether, soluble in alcohol and in alkalis, precipitable by gelatin, ferric oxide, and lead salts (Peckolt, *Arch. Pharm.* [2] cviii. 142).

DRUPOSE. $C^{12}H^{20}O^{8}$ (J. Erdmann, *Ann. Ch. Pharm.* cxxxviii. 1).—A substance produced, together with glucose, by the action of boiling moderately diluted hydrochloric acid on glycodrupose, the stony concretions found in pears:

$$\underset{\text{Glycodrupose.}}{C^{24}H^{36}O^{16}} + 4H^{2}O = \underset{\text{Drupose.}}{C^{12}H^{20}O^{8}} + \underset{\text{Glucose.}}{2C^{6}H^{12}O^{6}}$$

It is a greyish-red body, similar in structure and physical properties to glycodrupose. By boiling it with dilute nitric acid, and treating the residue with water, ammonia, and alcohol, yellowish-white granules are obtained, which dissolve in cuprammonia, and exhibit the composition and properties of cellulose, probably thus:

$$\underset{\text{Drupose.}}{C^{12}H^{20}O^{8}} + O^{2} + H^{2}O = \underset{\text{Cellulose.}}{C^{6}H^{10}O^{5}} + \underset{\text{Glucose.}}{C^{6}H^{12}O^{6}}$$

Glycodrupose. $C^{24}H^{36}O^{16}$.—The stony concretions in pears, produced by thickening and hardening of the cell-walls, consist of this substance, together with a small quantity of mineral matter. To obtain it, the pears, after prolonged boiling with water, are converted into a thick pulp by rubbing them through a metal sieve, and the concretions which settle to the bottom on mixing this pulp with a large quantity of water are purified by digestion with dilute acetic acid, washing with water, and treatment with alcohol and ether. It forms small grains of a faint yellowish-red colour, which when heated on platinum foil, burn away without previous fusion. When heated in a tube, it yields an acid distillate and pungent vapours. When boiled with alkalis, it turns brown; with dilute acids, red. On triturating it with strong sulphuric acid, and boiling the diluted solution for some time, a liquid is obtained which reduces cupric oxide in alkaline solution. Glycodrupose is insoluble in water, alcohol, ether, chloroform, benzol, carbon bisulphide, alkalis, cuprammonia, and most dilute acids, partially soluble in dilute nitric acid. When boiled with this acid, it yields cellulose, but less abundantly than drupose; also a small quantity of oxalic acid and dark-coloured humous products.

DUFRENITE. See Phosphates.

DUODECYL COMPOUNDS. Also called *Lauryl compounds. Duodecane* or *Duodecyl Hydride*, $C^{12}H^{26}$, is one of the constituents of American petroleum. It boils at 196°–200°, has a faint odour of turpentine, and is attacked by a mixture of nitric and sulphuric acids at the boiling heat, yielding a crystallisable and an oily body, together with volatile acids. *Duodecyl chloride*, $C^{12}H^{25}Cl$, is a faintly yellowish, nearly inodorous liquid, boiling at 242°–245°, and of sp. gr. 0·933 at 22° (Pelouze a. Cahours, *Jahresb.* 1863, p. 530).

Duodecylene, $C^{12}H^{24}$, is one of the hydrocarbons obtained by Warren and Storer by destructive distillation of the lime-soap of Menhaden oil; also from Rangoon tar. It has a sp. gr. of 0·8361 at 0°, and boils at about 212° (*Zeitschr. f. Chem.* [2] iv. 230).

DURENE. *Tetramethyl-benzene.* $C^{10}H^{14} = C^{6}H^{2}(CH^{3})^{4}$.—See Methyl-Benzenes, under Methyl.

E

ECGONINE. $C^9H^{15}NO^3$.—A base obtained by heating cocaïne with hydrochloric acid. (See Cocaïne, p. 479.)

EGG. *Analysis of the Yolk* (J. L. Parke, *Med.-chem. Unters.* i. 209; *Jahresb.* 1867, p. 776).—The yolk separated from the white was exhausted with ether till the decanted liquid appeared colourless; the residue was then treated with alcohol at 45°–50°, and filtered warm. The substances remaining on the filter (albuminoïds and inorganic salts) were washed with water to remove soluble salts; the undissolved portion was dried, weighed, and incinerated; and the weight of the ash determined. The ethereal and alcoholic extracts freed from ether and alcohol by distillation in a vacuum were dried over sulphuric acid; and the residues, after being weighed, were separately saponified by boiling for about seven hours with strong alcoholic potash solution.

a. The saponified residue of the ethereal extract, after the ether had been completely expelled over the water-bath, was dissolved in water (at least a litre to 40 grm. of yolk), and agitated with ether to dissolve out the cholesterin; the remaining aqueous solution, after supersaturation with hydrochloric acid, yielded to ether the fatty acids, which were dried in a rarefied atmosphere. In the evaporated and aqueous solution the phosphoric acid was determined by fusion with sodium carbonate and nitre.—*β*. The residue of the alcoholic extract, saponified with alcoholic potash, and freed from alcohol by evaporation, was dissolved in a small quantity of water and supersaturated with hydrochloric acid; the fatty acids thereby separated were filtered off and determined directly; and the phosphoric acid was estimated in the filtrate.

100 pts. of yolk thus treated yielded:

	A Fresh Yolk	B On the 10th day of incubation	C On the 17th day of incubation
Ethereal extract:	31·391	23·542	35·417
containing { Cholesterin .	1·750	1·281	1·461
containing { Fatty acids .	25·953	19·560	29·513
containing { Protagon (calc.)	17·422	13·509	17·981
Alcoholic extract:	4·826	4·039	4·516
containing { Fatty acids .	2·949	2·232	2·746
containing { Protagon (calc.)	10·031	8·019	9·362
Soluble Salts . . .	0·353	0·287	0·430
Albuminoïds	15·626	14·201	13·942
Insoluble Salts . . .	0·612	0·623	0·908
Total of Solid Matter . .	52·808	42·692	55·213

The quantity of protagon calculated from the phosphoric acid directly determined, amounts, in the alcoholic extract, to more then the total weight of the latter, showing that another substance richer in phosphorus must also be present. This conclusion has been confirmed by Hoppe-Seyler (*Med.-chem. Unters.* i. 215), who finds that the portion of the yolk which is insoluble in ether, consists of a whitish, pasty, flocculent mass, which is dissolved by a solution of common salt to a clear-filtering liquid, and may be precipitated therefrom by a large excess of water and a few drops of acetic acid. The same substance is more easily obtained in a similar manner from caviare (the salted roe of the sturgeon). If the substances precipitated by water be treated with alcohol of 40°–50°, and the liquid filtered warm, it leaves on evaporation a substance very much like protagon, which swells up in water, is precipitated by sodium chloride from the swollen mass, but always remains soft and forms oily drops. This is the phosphoretted compound in question; it appears to be identical with lecithin (iii. 566); it is moderately soluble in alcohol, and separates from the saturated alcoholic solution when cooled below 0° in groups of slender silky needles. Ether containing water also separates crystalline globules from the alcoholic solution. The portion of the yolk which is insoluble in alcohol consists of salts and albuminous substances, which latter are insoluble in solution of common salt, and are coagulated thereby. They are identical with the so-called vitellin, and contain on the average 0·75 p. c. sulphur, but no phosphorus if the exhaustion with alcohol has been complete. The vitellin exists in the yolk in combination with the phosphoretted substance (lecithin), the combination being broken up by treatment with alcohol, which dissolves the phosphoretted body (see also Diakonow, *Med.-chem. Unters.* i. 221; *Jahresb.* 1867, pp. 774, 778).

Colouring Matter of the Yolk.—The ethereal extract of the non-coagulated yolk of hens' eggs yields on evaporation a yellow residue consisting of fat and colouring matter. After saponification with soda-ley, the colouring matter may be extracted from the saponified mass by agitation with ether, showing that yolk of egg does not contain any colouring matter of bile, since the sodium-compound of bilirubin is insoluble in ether. The ethereal solution just mentioned leaves on evaporation a deep golden-yellow fat, non-saponifiable or difficult to saponify, which gradually solidifies to a buttery mass in consequence of the separation of cholesterin. This fat, comparatively rich in colouring matter, is very much like the fat containing hæmatoïdin which occurs in the ovaries. It is coloured pure blue by slightly concentrated nitric acid; dissolves with golden-yellow colour in ether and chloroform; and the solution previously mixed with alcohol is decolorised by nitric acid containing nitrogen tetroxide, without any previous play of colours. With carbon bisulphide an orange-coloured solution is obtained. Ammonia does not remove the colouring matter from its solution in chloroform. These properties seem to show that the colouring matter of egg-yolk is either hæmatoïdin or a body nearly allied thereto (Städeler, *J. pr. Chem.* c. 148).

Amylaceous Substance in Egg-yolk.—According to C. Dareste (*Compt. rend.* lxiii. 1142), egg-yolk contains a considerable quantity of microscopic granules, which turn blue with iodine, and in form and structure are very much like starch. They are mostly very small, but a few are as large as the granules of wheat-starch. With the development of the embryo this amylaceous substance gradually disappears.

Egg-shells.—W. Wicke (*Ann. Ch. Pharm.* cxxv. 78) has analysed the egg-shells of several birds, with the following results:

	Heron	Gull	Pheasant	Goose	Hen	Duck
Calcium Carbonate .	94·60	91·96	93·33	95·26	93·70	94·42
Magnesium „ .	0·69	0·76	0·66	0·72	1·39	0·50
Phosphates	0·42	0·83	1·37	0·47	0·76	0·84
Organic Substances .	4·30	6·45	4·64	3·55	4·15	4·24

Wicke also finds that the colouring matters of egg-shells are identical with the green and brown colouring matters of bile (*Jahresb.* 1859, p. 642).

From experiments by Roussin (*ibid.* p. 640) on hens fed for several days before laying, with potatoes and oats, to which different mineral salts were added, it appears that the calcium carbonate in the normal shells may be more or less replaced by isomorphous salts, such as the carbonates of barium, strontium, and even of lead, but especially by magnesium carbonate. When alkaline bromides and iodides were added to the food, the alkaline chlorides in the white and yolk of the egg were partly replaced by these salts. The increase in the proportion of bromide or iodide was however attended with a diminution of the calcareous envelope, which ultimately disappeared altogether, leaving the egg surrounded only by a membrane. The addition of calcium arsenate to the food was fatal to some of the hens; nevertheless arsenic was found in the egg-shells.

H. Rose (*Pogg. Ann.* cxvii. 627) analysed a fossil egg-shell weighing 252 grams, found in the guano of the Chincha islands. The interior crystalline or slightly brownish mass contained, together with a small quantity of organic matter:

Potassium sulphate	Ammonium sulphate	Ammonium chloride	Sodium chloride	
70·59	26·55	1·25	0·65	= 99·04.

The mass contained therefore 2 mol. potassium sulphate to 1 mol. ammonium sulphate, by which salts the original constituents of the egg had been replaced. The still remaining portion of the original shell contained in 100 pts.:

CO^2	SiO^2	Org. matter	K^2O	Cl	CaO	$(PO^4)^2Ca^3$
0·91	0·45	2·07	2·33	8·84	0·34	77·82.

In the interior of the egg there was found at one part a small quantity of black humous substance soluble in potash.

EKMANITE. A hydrated ferrous silicate containing manganese and magnesium, occurring in dense finely laminated veins and bands in the iron mine of Brunsjö, in Grythyttan, Sweden. It varies somewhat in structure and composition, but the general result of the analysis leads to the formula $4MO.3SiO^2 + 3H^2O$ (L. J. Igelström, *Jahresb.* 1867, p. 995).

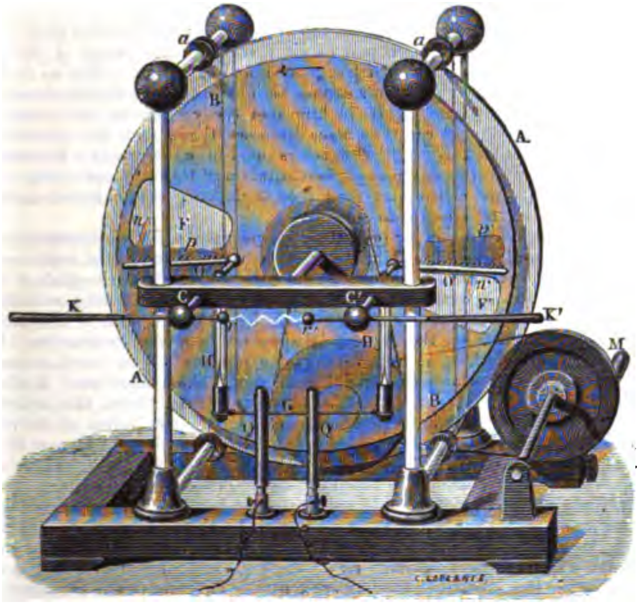
ELAÏDIC ACID. $C^{18}H^{34}O^2$.—This acid, like oleic acid, unites directly with bromine, without elimination of hydrobromic acid, forming the compound $C^{18}H^{34}Br^2O^2$, isomeric (or identical?) with dibromostearic acid. It is a white crystalline acid soluble in alcohol and ether, melting at 27°. It is monobasic; the barium salt is gummy and friable. By sodium-amalgam it is reconverted into elaïdic acid (Burg, *Bull. Soc. Chim.* [2] iii. 191).

ELALDEHYDE. See ALDEHYDE (p. 76).

ELECTRICITY. Holtz's Electrical Machine (Holtz, *Pogg. Ann.* 1865, cxxvi. 157; *Phil. Mag.* [4] xxx. 425; *Ann. Ch. Phys.* [4] viii. 201.—*Pogg. Ann.* cxxvii. 320; cxxx. 128, 168, 287; *Ann. Ch. Phys.* [4] xiii. 440.—*Pogg. Ann.* cxxxvi. 171; *Ann. Ch. Phys.* [4] xvii. 503. Poggendorff, *Pogg. Ann.* cxxxiv. 304; cxxxix. 158. Riess, *Pogg. Ann.* cxxxi. 215; cxl. 168, 276. F. Kohlrausch, *Pogg. Ann.* cxxxv. 120).—This is a contrivance by which a very small initial charge is made to give rise to an indefinitely great quantity of electricity of high tension; its action may be described in general terms as equivalent to that of an electrophorus and a condenser combined together in such a way as to act upon each other alternately, the condenser being first charged by the electrophorus, then reacting upon it so as to increase the charge of the cake; next being charged by the electrophorus to a higher degree and reacting upon it more strongly than before; and so on, the charge of each becoming gradually greater and greater until the insulation is overcome. The form usually given to the machine is shown in fig. 11. Its construction is as follows: A circular plate of thin and very flat glass, B B, is mounted upon an insulating ebonite axle, so that it can rotate in a vertical plane, and a second glass plate, A A, also as thin and flat as possible, is fixed parallel to it, with its centre in the same horizontal line, and at a very short distance (⅛ to ¼ inch) from it. At the middle of the fixed plate there is a round hole, through which the axle of the movable plate can pass without touching, and there are two deep notches or *windows*, F F′, cut out at opposite ends of a diameter; at the back of the glass (that is, on the side turned *away* from the rotating plate) a piece of paper, *p*, about two inches broad is pasted along the lower edge of one of these openings, and a similar piece, *p′*, is pasted along the upper edge of the other opening, each of these pieces of paper having projecting from it a couple of tongues of stiff paper, *n n′*, long enough to project through the opening and just touch the movable plate; both the papers and their projecting tongues are well varnished. On the side of the movable plate which is farthest away from the fixed plate, and opposite to the two pieces of paper just mentioned, are two collectors, O O′, each consisting of a row of metal points projecting from an insulated metal arm to within a very small distance of the rotating plate. These collectors are connected with the main conductors of the machine, C C′, each of which is provided with a movable discharging rod, K K′, by means of which they can at will be placed in electrical connection with each other, or separated by any required interval. In order to put the machine in action, the two conductors are connected together, the movable plate is set rotating at a moderate speed, and while it is moving, an electrified body, such as a piece of ebonite excited by friction, or the cover of an electrophorus, is brought near to, or into contact with, one of the paper armatures. Both the papers then rapidly become strongly charged with opposite kinds of electricity, and if the knobs, *r r′*, of the discharging rods are separated to a short distance, a stream of sparks is seen to pass between them. These sparks become less frequent, but larger and brighter, if each of the conductors is connected with the inside coating of an uninsulated Leyden jar. The sparks also increase in size, but diminish in frequency, when the discharging knobs are moved farther apart, but if the distance between them is made greater than a certain limit, depending chiefly upon the insulation of the different parts of the machine, the sparks cease to pass altogether, and, unless the knobs are quickly brought nearer to each other, the machine soon ceases to act.

The action of the machine may be explained, at least as to its general features, as follows. Suppose a positive charge to be given to one of the paper armatures: then, at all points in the neighbourhood of the paper, there will be a force acting which tends to drive positive electricity away from it, and to draw negative electricity near; and this force, acting successively upon each portion of the rotating plate as it passes between the paper and the points of the collecting comb, will, if sufficiently powerful, cause positive electricity to escape from the plate into the points, and negative electricity to escape from the points upon the plate. In consequence of this action, the comb of the second conductor (which, as we have said, is, to begin with, in metallic connection with the first) becomes positively electrified, while each portion of the glass plate passes the comb of the first conductor negatively electrified. But before any given part of the plate comes opposite to the points of the second conductor, its back is grazed by the tongues projecting from the second paper armature, and therefore negative electricity is repelled into this armature by the negative charge upon the front surface of the plate: in this way, the second armature gradually acquires a negative charge. We now have, at the second side of the machine, what may be called a stream of glass flowing between a negatively electrified piece of paper and the positively electrified points of the second collecting comb; hence positive electricity escapes from the points upon the glass, and negative electricity passes from the glass into the points, and consequently the glass passes this row of points positively charged. Then, returning to the first side of the machine, we have the glass arriving opposite the tongues of the first armature with a charge of the same kind (positive) as this armature has already got, but of higher tension (because it is due to the inductive action of this armature aided by the condensing effect of the opposite charge upon the other armature), and therefore able to strengthen the original charge of the paper. Next, the glass passes between this more strongly charged armature and the corresponding row of points, which now give up negative electricity to it, not only in consequence of the inductive action of the charge upon the first piece of paper, but also of the reaction of the negative charge upon the second paper. Consequently, the glass passes the first row of points with a stronger negative charge than it had at first,

FIG. 11.



and therefore strengthens the charge of the second paper armature, which in its turn reacts more powerfully than before upon the glass, as it passes between it and the now more strongly positive row of points of the second conductor, and so causes it to return to the first armature with a stronger positive charge than before. In this way, as the rotation continues, the two pieces of paper on the fixed plate become more and more strongly charged with the opposite electricities, and therefore exert a stronger and stronger inductive action upon the rotating plate as it passes between them and the collecting combs. Supposing, for the sake of distinctness, that the side of the machine to which the positive charge is first given is the side on which the motion of the revolving plate is upwards, the action may be described in general terms as consisting in the convection of negative electricity from the first collecting comb to the second by the upper half of the revolving plate, and the convection of positive electricity in the opposite direction by the lower half; and since the motion of negative electricity in one direction is the same thing as the motion of positive electricity in the opposite direction, the action of both halves of the plate may be described as causing the transfer of positive electricity from side to side, in the direction of the motion of the lower half, which is compensated by a corresponding flow of positive electricity in the opposite direction through the conductors. It is this last-mentioned current which shows itself as a stream of sparks when the discharging rods of the conductors are separated.

From this explanation of the action of the apparatus, it will be seen that it depends essentially upon the charge of each part of the revolving plate being of the opposite sign to that of the armature which it last passed, and of the same sign as that of the one which it is approaching; but this cannot be, unless there is electrical communication between the two conductors. If the knobs of the conductors are separated too far, no electrical interchange can take place between them, and the armatures then represent two oppositely charged conductors of limited capacity, between which portions of glass are continually passing backwards and forwards conveying a part of the charge of each to the other, and thus soon equalising them: hence under these circumstances the machine ceases to act.

In order to charge a Leyden jar or battery by means of a Holtz's machine, it should be placed on an insulating support, and one of the coatings connected with one of the conductors, and the other with the other; or two jars may be charged at once by connecting their outer coatings together and connecting each conductor with the inner coating of one jar. The figure shows two small Leyden jars, H and H′, whose outer coatings are connected by the wire G, suspended from the conductors. By this arrangement of course the jars receive opposite charges. Some care is needed in trying to charge a jar to the highest point with one of these machines: if the knobs *r r′* are so far apart that a spark is unable to pass between them, the action of the machine ceases when the jar is charged so highly that the two halves of the revolving plate are no longer charged by the inductive action of the armatures they have respectively last passed, as highly as the armatures which they are approaching; and if the movement of the machine be continued beyond this point, the charge which the jar has already got will be destroyed; on the other hand, if the discharging knobs are nearer together, the jar is apt to be discharged by them before it has acquired as high a charge as might be given to it. To remedy this inconvenience, Riess adds to the machine a third paper armature, with a third collecting comb opposite to it, half-way between the two armatures already spoken of. This additional armature has no projecting point, but is connected, by a strip of paper pasted along the edge of the fixed plate, with the armature which precedes it in relation to the direction of rotation of the revolving plate, and the additional collector is in metallic connection with the conductor which follows it, and likewise with the ground. The inner coating of the jar or battery to be charged is connected with the conductor which still remains insulated, and the outer coating is connected with the ground. The action of these additional parts is easily understood if we bear in mind that the additional armature is equivalent to an extension of the one with which it is connected, and that the additional collector takes the place of the one connected with the jar when this one has ceased to act in consequence of the jar being fully charged. The writer of this article has found that a Leyden jar may easily be charged to a high degree by a machine of the construction shown in fig. 11 (p. 551), if the jar is first insulated, one coating connected with one of the paper armatures, and then a conductor connected with the other armature, gradually brought near, and finally into contact with the other coating. During this process, the discharging knobs *r r′* should be at a moderate distance apart, and a stream of sparks should pass freely between them.

The electric current through a wire connecting the conductors of a Holtz's machine has been shown by Poggendorff to be independent of the resistance of the circuit, and by F. Kohlrausch to be sensibly proportional to the velocity of rotation. The latter found that a plate 40 centimetres in diameter, revolving 5 times in 3 seconds, produced a constant current capable of decomposing water at the rate of 3½ millionths of a milligramme per second, or equal to that of a Grove's cell in a circuit of 48,000 mercurial units (about 45,000 B. A. units) resistance.

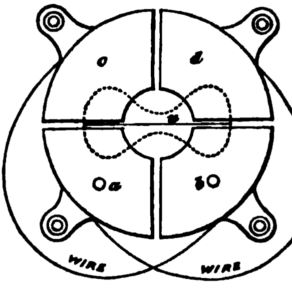
Besides the machine which has been described, Holtz has constructed machines acting upon the same general principle, but differing from this one considerably in arrangement; the construction has also been varied and simplified by Poggendorff, his most important alteration being the substitution of small holes, just large enough to let the tongues of the paper armatures pass through, for the large openings of Holtz's original form.

An electrical machine, acting essentially upon the same principles as Holtz's, but in which the inductive action is exerted upon sheets of tin-foil carried by revolving glass plates, was constructed by Töpler of Riga (*Pogg. Ann.* cxxv. 469; *Ann. Ch. Phys.* [4] viii. 313) at about the same time that the first machines were made by Holtz; but it has not yet come into such general use, and does not seem to have been made to yield such powerful effects as those that have been obtained from machines of the kind we have just described. A machine analogous in many respects to that of Holtz has also been recently described by Poggendorff (*Pogg. Ann.* cxli. 161); and a self-acting arrangement, nearly equivalent to Töpler's machine, but with a stream of water, instead of tin-foil, as the moving conductor, has been constructed by Sir William Thomson (*Proc. Roy. Soc.* xvi. 67).

Thomson's Electrometers. Several different forms of electrometer have been recently devised by Sir William Thomson, which are much more sensitive and accurate than any that had been constructed previously. For details respecting these instruments, we must refer to Professor Thomson's description of them (*Rep. Brit. Assoc.* 1867, p. 489): here we can only give the general principle of two of the most generally useful forms—the 'Quadrant Electrometer' and the 'Portable Electrometer.'

The most important part of the Quadrant Electrometer, and that from which it takes its name, is shown (as seen from above) in fig. 12. It consists of four quarters of a flat circular box of brass, with circular apertures in the centres of its top and bottom, each of the quadrants being supported by a glass stem. The alternate quadrants *a* and *d*, *b* and *c*, are connected by wires so as to form two pairs, as shown in the figure, and one of the two bodies whose electrical states are to be compared, such as the terminals of a galvanic battery, or the earth and any body supposed to be positively or negatively electrified, is put into electrical connection with each pair. The indications of the instrument are due to the movements of a broad needle, *u*, of thin sheet aluminium, which is electrified and suspended inside the box formed by the four quadrants by an insulating fibre of silk. If all the quadrants are in the same electrical condition, and the needle is suspended quite symmetrically within them, it is evident that it will be in equilibrium when its axis is in the same vertical plane with one of the diameters of the box; but if the alternate quadrants are differently electrified, each end of the needle will be repelled by the two which are electrified in the same way as itself and attracted by the other two, and it will thus be subject to a couple tending to set it oblique to the position shown in the figure. In order to render the smallest motion of the needle visible, a small and very light concave mirror is fixed to a platinum wire which passes through it and reflects the light of a lamp, which is allowed to fall upon it through a narrow slit, upon a divided scale at a distance of about a metre. In the instruments first made, the needle was caused to come to rest in the zero position by the directive force of a minute magnet fastened to it and acted on by a larger steel magnet outside the case of the electrometer; but in the most recent instruments, the directive force of a bifilar suspension by two fine silk fibres is substituted for that of the magnet. The insulation of the quadrants of the needle is made as perfect as possible by enclosing them in a glass jar containing a quantity of strong sulphuric acid at the bottom. The outside of this jar is partially coated with tinfoil, which, with the sulphuric acid inside, converts it into a Leyden jar: this serves to increase the electrical capacity of the needle,

FIG. 12.



and so to make it retain for a long time a nearly constant electrical condition. Electrical connection between the needle and the sulphuric acid forming the inner coating of the jar is made by means of a small platinum weight, suspended in the acid by a very fine platinum wire attached to a stouter platinum wire passing through the needle, an arrangement which also diminishes very much the oscillations of the needle.

In the *Portable Electrometer*, the body whose electrical state is to be tested is connected with an insulated brass disk, opposite the middle of which is a small square plate of aluminium, fixed to the shorter arm of a light lever of the same material, and kept at a constant electrical charge by being connected with the inner coating of a Leyden jar. The measurement is made by observing, by means of a suitable micrometric arrangement, the distance at which the disk exerts a given attractive force upon the aluminium plate. In using the instrument, an 'earth-reading' is first taken, by observing the position of the disk in which it exerts this force when both the disk and the outer coating of the Leyden jar are connected with the earth. Then the earth-reading, subtracted from the reading obtained when the disk is connected with the body to be tested, gives the electrical difference between this body and the earth expressed in terms of an arbitrary scale, the value of which can be ascertained, if required, by a special experiment with two bodies whose electrical states differ by a known amount. It is an obvious precaution, in order to obtain great accuracy, to take a second earth-reading, after making the experiment with the body to be examined, and if this differs from the first, to estimate the most probable earth-reading for the moment of the experiment with the body in question.

New forms of Galvanic Battery. Many attempts have been made to construct a galvanic cell which should combine the good qualities of the older forms of constant batteries (such as Daniell's, Grove's, Bunsen's) with greater convenience in use and the absence of the necessity for frequent examination or renewal; we will briefly describe a few of the newer forms.

1. *Walker's Platinised Carbon Battery.*—This is simply a modification of Smee's battery (ii. 427) in which the platinised platinum or silver is replaced by a plate of platinised gas-carbon. The carbon plates are platinised by being made for a short time the negative electrode in a weak solution of platinic chloride in dilute sulphuric acid. A battery of this construction, although in proportion to its size much cheaper than one of Smee's, appears to be at least equal to it in efficiency (C. V. Walker, *Phil. Mag.* [4] xviii. 73).

2. *Bichromate of Potassium Battery.*—When a battery of small resistance but considerable electromotive force is required occasionally, amalgamated zinc and gas-carbon, immersed in a solution of equal weights of potassic bichromate and hydric sulphate in about twenty times their weight of water, forms a very convenient combination. As the solution gradually attacks the zinc, even when the circuit is not completed, the zinc plate in cells, constructed on this principle, is generally fixed to a brass rod by which it can be drawn up out of the liquid or let down to any depth between two parallel plates of carbon.

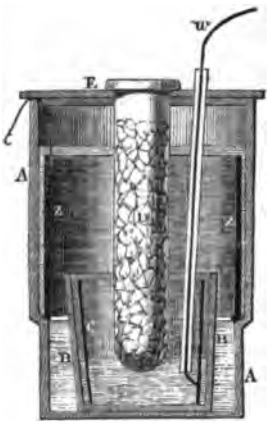
3. *Chloride of Silver Battery.*—Messrs. Warren De la Rue and Hugo Müller (*Chem. Soc. J.* xxi. [new series, vi] 488) recommend, as a compact and convenient battery for use in cases where several hundred small cells are required to give a great electromotive force, one of the following construction: The electro-positive plates consist of pieces of Belgian zinc wire (English zinc being too impure for the purpose) $2\frac{3}{8}$ inches long and 0·2 inch in diameter; the electro-negative plates are formed by pieces of pure silver wire 0·03 inch in diameter, round which is cast a cylinder of silver chloride 0·22 inch in diameter. The silver wire projects about a fifth of an inch below the bottom of the cylinder of chloride and about an inch and a half above the top, so as to allow of its being connected with the zinc of the next cell. The liquid used is a solution of common salt in distilled water, 25 grammes to the litre (or 219 grains to the pint). A battery of this construction may be left to itself for weeks together, if the poles are not connected, without other injury than the evaporation of water. From the size of the plates employed, it is evident that its resistance must be very considerable; its electromotive force is about equal to that of a Daniell's cell (see p. 579).

4. *Sulphate of Mercury Battery.*—This may be described as a Bunsen's battery, in which the nitric acid is replaced by mercurous sulphate. As usually made, the zinc plate is in the form of a hollow cylinder, surrounding a porous vessel containing a rod of gas-carbon, and filled up with powdered mercurous sulphate and enough water to make it into a thick mud; outside the porous vessel and in contact with the zinc is dilute sulphuric acid. This battery, which was proposed by Marié-Davy, is recommended

as being very constant and requiring little supervision. It has come into use to some extent for telegraphic purposes (Wiedemann, *Galvanismus*, p. 271).

5. *Binoxide of Manganese Battery.*—This is another zinc and carbon battery, but the porous cell containing the carbon plate is filled up with a mixture of binoxide of manganese in coarse powder and small fragments of gas-carbon, the object of which is to increase the conductivity. Only one liquid is employed, namely a saturated solution of sal-ammoniac; the electro-positive metal is amalgamated zinc. Cells of this construction are said by the inventor, M. Leclanché, to remain in working order for months, or even a year, together, without requiring other attention than the occasional replacement of the water which has evaporated. It is extensively used for telegraphic purposes in France.

FIG. 13.



6. *Meidinger's Battery.*—This is a modification of Daniell's battery, and differs from the common form of it only in the arrangement of the parts and in not having any porous partition between the copper and zinc plate. Its construction will be understood by reference to fig. 13,* where A is a glass vessel 170 mm. high and 100 mm. wide at the bottom and to a height of 60 mm. from it; above this height it is 110 mm. wide, and on the shoulder, formed by the junction of the narrower part with the wider, rests the cylinder of amalgamated zinc, z, 90 mm. deep. Another slightly conical glass vessel, B, 75 mm. high, 65 mm. wide at the bottom and a little wider at the top, is cemented inside A, and contains a cylinder of sheet copper, c, to which is fixed a copper wire, *w*, insulated where it passes through the liquid by a glass tube or a covering of gutta-percha. A wide glass tube, D, contracted before the lamp so as to leave only a small opening at the bottom, which is about 20 mm. from the bottom of the vessel B, is supported by the cork or wooden lid E, and is nearly filled with crystals of sulphate of copper.

The liquid with which the cell is charged is a solution of sulphate of magnesia in rain or distilled water, from 50 to 125 grammes of the commercial salt being allowed for each cell. This liquid, entering the tube containing the sulphate of copper, forms a saturated solution which collects at the bottom of the vessel B in contact with the lower part of the copper plate. It is evident that such a cell cannot be moved about without danger of mixing the solutions, but when left at rest it is very constant (Meidinger, *Pogg. Ann.* cviii. 602). A simplified form of Meidinger's battery has been described by Pincus (*Jahresb. f. Chem.* 1868, p. 99).

7. *Sir William Thomson's Battery* (*Proc. Roy. Soc.* [1871] xix. 253; *Chem. Soc. J.* xxiv. 102).—This is another Daniell's battery in which the porous diaphragm is dispensed with. The cell is a round or rectangular glass jar with a flat bottom, which should be 10 centim. or more in depth, when permanence and ease of management are of more importance than very small internal resistance. A disk of thin sheet copper is laid upon the bottom of the cell, with a copper wire, insulated with gutta-percha, fastened to it to serve as electrode. A grating of zinc, also provided with an electrode, is supported in the upper part of the jar. A glass tube (the *charging tube*) a centimetre or more in internal diameter, expanded to a funnel at the top, is supported so that its lower open end may be about one centim. above the copper. A glass siphon, with a cotton-wick core, or a capillary glass tube, is placed so as to draw liquid gradually from a level about 1½ centim. above the copper, and to discharge it at a level slightly higher than the upper surface of the zinc. To put the cell in action, the jar is filled with semi-saturated solution of zinc sulphate, and finely broken crystals of copper sulphate are placed in the funnel at the top of the charging tube. To keep the cell in working order, pure water, or water one quarter saturated with zinc sulphate, should be added from time to time to replace that drawn off by the siphon, so as to keep the liquid in contact with the zinc about half saturated with zinc sulphate.

8. *Siemens and Halske's Battery.*—Messrs. Siemens and Halske have also introduced a modified form of Daniell's battery, intended to remain in action for a considerable

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* Drawn to a scale of ¼.

time without requiring attention. It is more complicated than Meidinger's and requires a porous cell of peculiar form: for a description and figure we must refer to *Pogg. Ann.* cviii. p. 608.

It is impossible to give any unqualified recommendation or condemnation of these or the many other batteries that have been proposed from time to time, since the qualities which are considered advantageous in a battery differ almost as much as the purposes to which it can be applied. Sometimes compactness is the chief thing to be aimed at, sometimes cheapness; sometimes it is needful to be able to produce a current of short duration at any moment, sometimes a current is wanted to be of nearly constant strength for days together; sometimes great electromotive force is required, and consequently a very large number of cells must be used (in such cases the chief desideratum is simplicity of construction, so that the labour of charging the cells may be as small as possible); and in other cases, again, other qualities assume the greatest importance. In most cases a little consideration of the chemical and mechanical structure of a galvanic cell will leave but little doubt as to whether or not it is suitable for any proposed purpose. For instance, it is obvious that cells in which the plates are small and far apart must have great internal resistance, and hence that a strong current can never be obtained from them, except by combining a great number of them abreast; again, if it is needful to leave a battery charged for days or weeks at a time, ordinary Grove's, Bunsen's, or Daniell's cells would be unsuitable, on account of the gradual mixture of the two liquids and consequent solution of the zinc which would take place: in such cases, Thomson's, Meidinger's, Marié-Davy's, or sometimes Leclanché's batteries might be used. In other cases—as, for instance, for the electro-deposition of metals, or whenever a strong current is to be maintained for a considerable time—it is essential that the capacity of the cells should be large compared with the size of the plates, in order that the amount of chemical action which takes place may not affect any very great proportion of the liquid or liquids with which the battery is charged. It must also be remarked further, in reference to the characters commonly ascribed to particular kinds of batteries, that the term 'constant battery' is frequently used in two very different senses. On the one hand, batteries are often called constant if they give a current of sensibly the same strength when their terminals are repeatedly joined for a short time by the same conductor at intervals of a few hours or days; whereas the proper meaning of the term constant, as applied to a battery, means that, if the poles are kept joined by a given conductor, a current of sensibly constant strength will be maintained for a greater or less length of time, and that, if the resistance of the circuit is altered, the strength of the current will alter in the inverse ratio. For a battery to be constant in the former sense, it is sufficient that there should be no local action when the poles are disconnected, and no spontaneous alteration due to the mixing of the liquids employed or other similar cause; these conditions are sufficiently fulfilled by Leclanché's and various other batteries, which are far from being constant in the true sense. Real constancy requires in addition that there should be no polarisation (ii. 429, 424), or, in other words, that the electromotive force should not vary with the strength of the current. Probably, properly constructed Grove's or Daniell's cells, of sufficient capacity, with well-amalgamated zinc plates, and with porous partitions sufficiently thick to prevent rapid mixing of the liquids, come nearer to possessing this kind of constancy of action than any other combinations that have been proposed hitherto. A table giving the comparative electromotive forces of several kinds of cells will be found at p. 579.

Thomson's Galvanometer. In the ordinary double-needle galvanometer (ii. 443, 444), the moment of inertia of the needles is usually considerable as compared with the moment of the deflecting couple due to a very weak current, and consequently the instrument is sluggish in its indications, and, if a current passes through it for only a very short time, may not even show any appreciable deflection; and again, when the astatic system has been deflected, its inertia prevents it from coming to rest again until after a considerable number of oscillations, and thus renders it impossible to make a series of observations in rapid succession with this instrument. If we try to remedy these defects by reducing the length of the needles, we run the risk of making the change of position due to a small angular displacement imperceptible. In these respects the galvanometer devised by Sir William Thomson is a very great improvement on the instruments previously in use. This is represented in its most complete form in fig. 14. A and B in this figure are two rather flat metallic bobbins filled with coils of fine copper wire, well insulated throughout its length, and wound in opposite directions upon each. The back and front of the bobbins are made in separate pieces, which when put together leave a small free space between them, as is shown in fig. 15, which represents a section of the bobbins and coils by a vertical plane passing through their axes. In this space is suspended by a silk fibre the astatic system of magnets M and N, each formed of a bit of fine watch-spring about ⅜ inch long, and connected by a thin strip of aluminium of such a length that one of the magnets is at the middle of each coil. In order to render the deflections of the

Fig. 14.

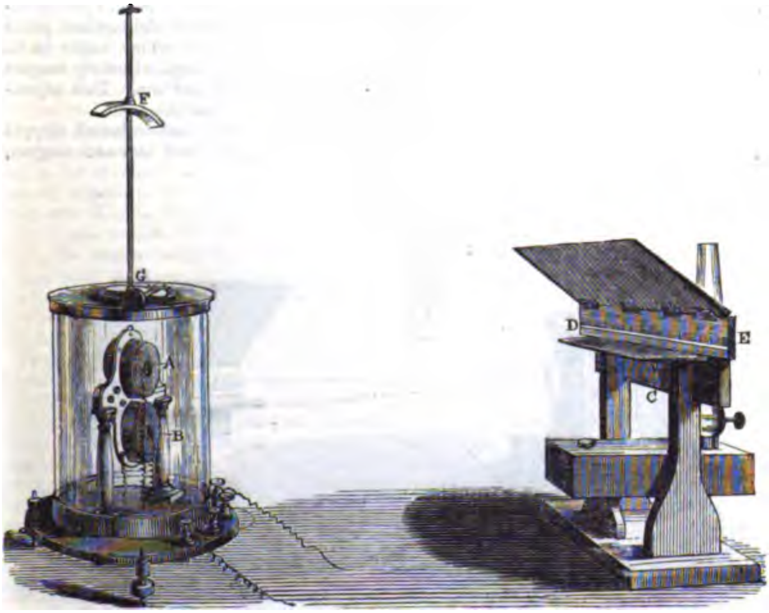
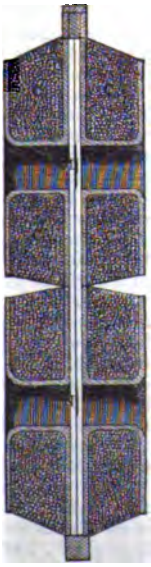


Fig. 15.



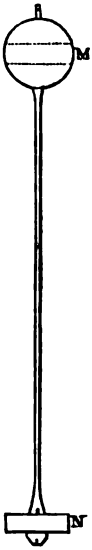
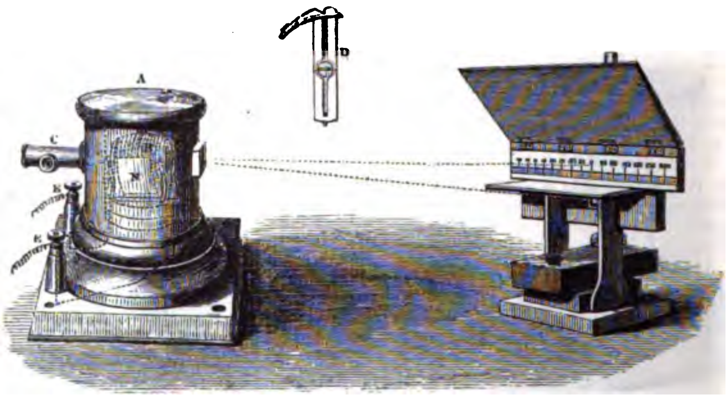


Fig. 16.

magnets perceptible, a small concave mirror of very thin silvered glass is fixed to the magnet inside the coil A (fig. 14), and reflects the light of a paraffin-lamp, which falls upon it through a narrow slit, C, so as to form an image of the slit upon the divided scale D E, at a distance of about three feet. This mirror, together with the two magnets and the connecting strip of aluminium, is shown in fig. 16 in its real size. All these parts are made so light that all together they weigh only about three grains. When no current is passing through the instrument, the axes of the suspended magnets ought to be perpendicular to the axes of the coils, and the image of the slit ought to be formed at the centre of the divided scale. In order to ensure the fulfilment of these conditions, the scale should be set at right angles to the vertical plane passing through the axes of the coils, and with its middle point, which ought to be directly over the slit, in this plane, and then the position of the large adjusting magnet F should be changed until the image appears in the required position. This adjustment can be made very accurately by means of the tangent-screw G.

Another form of the same instrument, specially intended for use on board ship, is represented in fig. 17. In this instrument there is only one coil and one magnet, and in order to counteract the effects of the ship's motion, the magnet and mirror are fixed to the middle of a silk fibre, which passes exactly through their common centre of gravity and is stretched from end to end of a brass slide (represented apart at D). This slide fits into a groove in the centre of the coil B, and the magnet is kept in an invariable position relatively to the coil, when no current is passing, by a broad steel horse-shoe magnet, N. The adjustment of the image of the slit to the zero-point of the scale is made in this instrument by means of a pair of straight magnets placed together with their like poles in opposite directions and contained in a brass tube at C: by means of a rack-and-pinion motion these magnets can be slid over each other in opposite directions, and thus can be made to neutralise each other entirely as to their action on the suspended magnet, or by making one of them project beyond the other the action of either can be made to preponderate to any required extent. Lastly, in order to counteract the local attractions due to the iron of the ship or of its freight, the instrument is enclosed in a thick casing of wrought iron, A.

Fig. 17.



It is easy to see that, with the scale at three feet from the mirror, the motion of the spot of light corresponding to any given angular deflection of the magnet will be equal to the tangent of twice the angle of deflection referred to a circle of three feet radius. This circumstance not only implies that very weak currents will produce sensible movements of the spot of light, but justifies us in concluding that currents which are not so strong as to send the spot of light beyond the end of the scale are proportional to the displacements they produce. Hence, for very weak currents a Thomson's galvanometer is an accurate measuring instrument. It can also be used for the comparison of stronger currents if, instead of allowing the whole current to traverse the instrument, some known proportion of it only, not too great to let the spot remain on the scale, be allowed to pass through it. For this purpose, a set of coils, technically called 'shunts,' generally adjusted so as to have respectively $\frac{1}{9}$, $\frac{1}{99}$, $\frac{1}{999}$ . . . of the resistance of the galvanometer-wire, are usually supplied with it by the makers. When one of these coils is put into the circuit, in multiple arc with the galvanometer, $\frac{9}{10}$, $\frac{99}{100}$, or $\frac{999}{1000}$ . . . of the current passes through the shunt, and only $\frac{1}{10}$, $\frac{1}{100}$, or $\frac{1}{1000}$ respectively through the galvanometer (see p. 565).

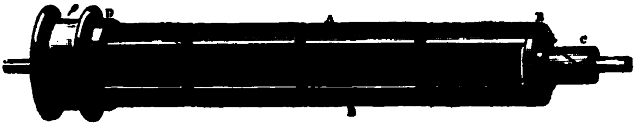
Magneto-electric Induction Machines. When a coil of wire surrounds an iron core, any alteration in the magnetic condition of the core produces an electromotive force in the wire; and if the coil forms part of a closed circuit, a current is produced in it the strength of which is proportional to the electromotive force, but inversely proportional to the resistance of the circuit. The magnitude of the electromotive force at any instant is proportional to the number of times the wire passes round the core, and to the rate at which the magnetic moment of the core is varying at that instant; consequently, the average electromotive force which acts in the wire during any given interval of time can be increased either by increasing the number of turns of wire forming the coil, or by increasing the magnetic change taking place in the core during the interval in question. If, however, we endeavour to increase the strength of the current, by augmenting the electromotive force in the former of these ways, a point is reached sooner or later beyond which any further addition to the length of the coil makes the current weaker instead of stronger; for, with a core of finite length, only a limited number of turns of wire can be placed in immediate proximity with it, and, if more wire is to be wound round it, the additional length must be arranged in one or more layers outside the first, and therefore of greater diameter, so that, after the first layer, the resistance of the circuit increases more rapidly than the electromotive force.

Applying these considerations to the construction of magneto-electric machines, we see that, other conditions being the same, that machine will give the strongest current in which the greatest length of wire is within a given distance from the core, and in which the changes in the magnetisation of the core are the most considerable.

These conditions are fulfilled much more perfectly in the form of magneto-electric machine devised by Siemens (*Pogg. Ann.* ci. 271 [1857]) than in the machines previously constructed, such as those described in vol. ii. pp. 455–457. The principal peculiarities of this arrangement are: first, that the soft iron keeper or armature, to the reversal of whose magnetism the induced currents are due, is magnetised transversely instead of longitudinally; secondly, that the action of the permanent steel magnets, instead of being concentrated upon the ends of the armature, is distributed over its whole length. Consequently, at each reversal of the magnetic polarity of the armature a much smaller coercive force has to be overcome than would be the case if the magnetisation were longitudinal; and the permanent magnets, being separated a short distance from each other, instead of being combined into one large magnet, retain their magnetism more completely.

A perspective view of a Siemens's armature is given in fig. 18, and a transverse section in fig. 20 (p. 560); a complete magneto-electric machine provided with one of these armatures is represented in the upper part of fig. 19, the ∩-shaped bodies P being the permanent steel magnets between whose poles the armature rotates. The armature itself is made by cutting two deep rectangular or semicircular grooves along the whole length of a cylinder of wrought iron, so as to leave the remainder with a transverse section approaching in shape to that of a dumb-bell, as shown in fig. 20. The wire forming the coil is wrapped longitudinally round the piece of soft iron, so as completely to fill the grooves, as represented in figs. 18, 20. A and B, in the former figure, are the surfaces of the iron core, which assume alternately north and south magnetic polarity, as it revolves between the poles of the fixed magnets; at C there is a commutator consisting of two pieces of steel, insulated from each other, each of which is connected with one end of the coil; D and E are brass collars which serve to keep the coil of wire in its place; and *p* is a pulley round which the driving belt works.

FIG. 18.



A very important improvement in the construction of magneto-electric machines, whereby they were made to produce effects greatly surpassing anything that had been previously obtained, and were in fact converted into the most powerful generators of dynamic electricity hitherto constructed, was made by Mr. Henry Wilde, of Manchester, in 1863 (*Patent* No. 3006, December 1, 1863; *Proc. Roy. Soc.* xv. 109 [1866]; *Phil. Mag.* [4] xxxii. 148). Without entering into details of

Fig. 19.

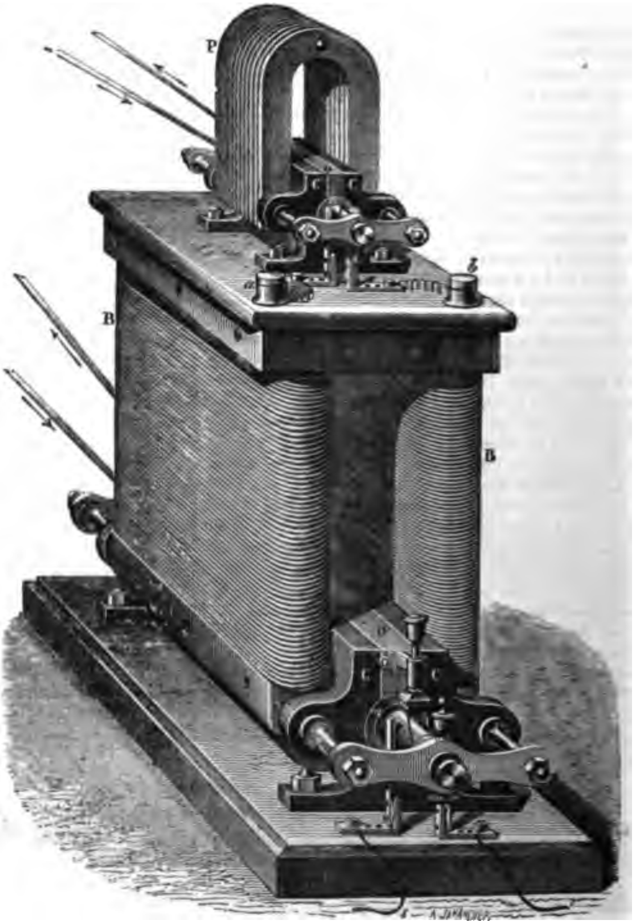
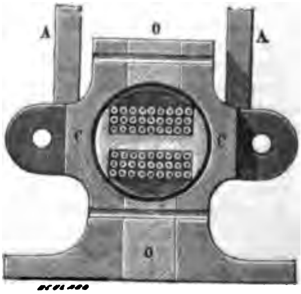


Fig. 20.



mechanical construction in connection with Wilde's machines, we may state the general principle of his invention to consist in the employment of the current produced by a magneto-electric machine, with an armature such as has been described, to excite an electro-magnet, and in using this electro-magnet to induce electric currents in the coil of a second armature of similar construction but larger size. Mr. Wilde was led to this mode of employing the current of the magneto-electric machine by the observation which he made that this current was capable, when used to magnetise soft iron, of producing electro-magnets of far greater power than the permanent magnets by which it was generated. Fig. 19 is a representation of a Wilde's magneto-electric machine: the upper part consists of a simple magneto-electric machine, and the lower part of a similar machine on a larger scale, with the substitution of the electro-magnets B B, excited by the current of the smaller machine on the top, for permanent magnets. The extremities of the magnets, in both the upper and the lower machine, rest upon two pieces of soft iron (c c, figs. 19, 20) of the same length as the armatures; these are hollowed out on the sides which are turned towards each other, so that, with the pieces of brass, o o, by which they are kept apart, they form two complete cylinders, within which the armatures revolve.

When once it had been ascertained that the current of a magneto-electric machine could be multiplied by causing it to excite an electro-magnet in a second machine, the further step of carrying the multiplication to a higher degree, by combining together three or more machines, was obvious. This step was made by Wilde, who used the current from a machine having six permanent magnets, each weighing 1 lb. and capable together of lifting about 60 lb., and an armature 1⅝ inch in diameter, to excite the electro-magnet of a second machine, having an armature 5 inches in diameter, while at the same time the current of the latter was made to traverse the electro-magnetic coils of a third machine, with an armature 10 inches in diameter. When the armatures of this triple machine were kept in rapid rotation by a powerful steam-engine, a current of enormous power was obtained from the third armature. When this armature was coiled with an insulated copper conductor 67 feet long and weighing 344 lb., and was driven at a uniform speed of 1,500 revolutions per minute, the current was sufficient to melt pieces of a cylindrical iron rod 15 inches long and ¼ inch in diameter, or an equal length of copper wire ⅛ inch in diameter. When the coil upon the armature consisted of a bundle of thirteen copper wires 376 feet long and weighing 232 lb., the same speed of revolution furnished a current which, when allowed to pass between rods of gas-carbon half an inch square, cast shadows of the flames of street lamps at a distance of a quarter of a mile, and produced upon ordinary photographic paper in 20 seconds a blackening effect equal to that produced by the full sunshine of a very clear March day in one minute.

The next step in the improvement of magneto-electric machines was made almost simultaneously by Drs. Werner and C. W. Siemens (*Proc. Roy. Soc.* xv. 367 [February 4, 1867]) and by Sir Charles Wheatstone (*Proc. Roy. Soc. ibid.* p. 369 [February 14, 1867]). The general principle involved in their improvements may be thus stated: If two pieces of soft iron, each of them slightly magnetised and surrounded by a coil of wire, both coils being connected so as to form parts of a single closed circuit, have their like poles moved towards each other or their unlike poles separated, a current will be induced in the coils in such a direction as to strengthen the magnetisation of the pieces of iron. And since this current will be proportional, other things being equal, to the strength of the magnetic forces which oppose the movement, and since these forces are themselves increased by the existence of the current itself, it is obvious that a continuous movement, under the conditions that have been indicated, must produce a current in the coils of continually increasing strength, even if the initial magnetism of the soft iron were indefinitely weak. In order to put this principle in practice, a magneto-electric machine was employed provided with soft iron electro-magnets and a Siemens's armature. If no current passed through the coils of the electro-magnet, and if the iron were quite unmagnetic, no current was produced by the rotation of the armature; but if a galvanic current be sent for a short time through the coils of the electro-magnet, the residual magnetism retained by the soft iron after the cessation of the current sufficed to produce a weak current, alternately in opposite directions, when the armature was made to revolve and the ends of the wire surrounding it were joined together. If now this current, after being reduced to a constant direction by a commutator, was made to traverse the coils of the electro-magnet in such a direction as to increase the slight magnetisation already existing, it was itself strengthened by the result of its own effect on the magnet, and in its turn increased still further the power of the magnet, and thus again its own strength. By the mutual action and reaction of armature and electro-magnet, 'the mechanical resistance is found to increase rapidly, to such an extent that either the driving-strap begins to slip or the insulated wires constituting the coils are heated to the extent of igniting their insulating silk covering' (Siemens).

But although currents of almost any degree of intensity can be produced by the arrangement that has been indicated, a magneto-electric machine constructed on this principle has the important practical defect that, in proportion as the current is employed in producing external effects, so the power of the machine to generate a current is lessened. A remedy for this was devised by Mr. Ladd (*Proc. Roy. Soc.* xv. 404), who adopted the simple expedient of putting two armatures into the same machine, and employing the current of one solely in maintaining the magnetism of the electro-magnets, while that of the other could be used for any other purpose. In machines of the largest size he places the armatures at opposite ends of a pair of broad electro-magnets (B B), as shown at *m* and *n*, fig. 21; in the smaller machines the armatures

FIG. 21.

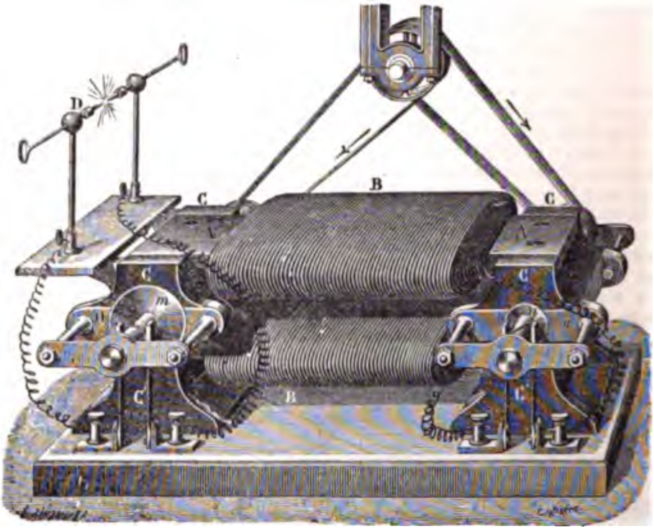
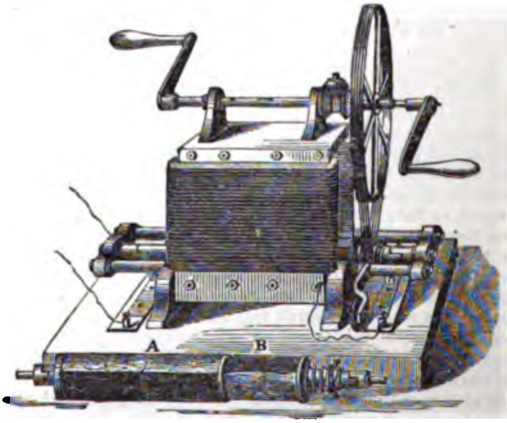


FIG. 22.



are connected together with their axes of rotation in the same straight line, and the coils are wound upon them at right angles to each other. A machine of this construction, intended to be driven by one or two men, is shown in fig. 22, and the double armature is represented separately at A B. (For a sketch of the mathematical theory of magneto-electric machines, see Maxwell, *Proc. Roy. Soc.* xv. 397. A good account of the construction and general principles of those above described is given by Bertin, *Ann. Chim. Phys.* [4] xv. 169.)

Electric Resistance of Conductors. The relations between the dimensions and the resistances of cylindrical electric conductors, such as metallic wires, stated at p. 466 of vol. ii., may be expressed mathematically as follows:

$$\rho = \mathrm{R}\frac{l}{a},$$

where ρ denotes the resistance of the particular conductor under consideration, l its length, a the area of its cross-section, and R a coefficient, called the 'specific resistance' of the material of the conductor. This coefficient expresses the resistance of a portion of the conductor having *unit length and unit section*, and has a constant value for the same material under the same conditions. It is frequently easier to determine by direct experiments the weight and specific gravity of a conductor, than the area of its cross-section, but the latter number can be easily calculated from the two former; thus, let w be the weight of the conductor, and s its specific gravity, or the weight of a portion of unit length and of uniform cross-section equal to the unit of area, then $a = \frac{w}{l\,s}$. Substituting this value of a in the last equation, we get

$$\rho = \mathrm{R}s\,\frac{l^2}{w},$$

which shows that the resistances of conductors of the same material are proportional to the squares of their lengths and inversely proportional to their weights.

In the case of a conductor having a circular section, such as a well-drawn wire, the area of the section may be calculated from a measurement of the diameter, which may be made either under a microscope or by means of a micrometer. Then, since, if d be the diameter, $a = \frac{\pi}{4}d^2$, the resistance of the conductor may be expressed in reference to its length and diameter thus:

$$\rho = \mathrm{R}\,\frac{l}{\frac{\pi}{4}d^2} = 1{\cdot}27324\,\mathrm{R}\,\frac{l}{d^2}.$$

The following table (p. 564), calculated from Matthiessen's determinations by F. Jenkin (*Journ. Soc. Arts*, February 23, 1866), gives the values of the products Rs and 1·2732 R for wires of several of the most important metals, expressed in terms both of the British and the metrical standards of length and weight, and referred to the unit of electrical resistance adopted by the Committee of the British Association on Electrical Standards.

An example will show the mode of using this table. For instance, let it be required to know the resistance at 0° C. of 240 feet of hard-drawn copper wire weighing 16½ lb. The first column of figures gives, for the resistance of 1 foot of wire weighing 1 grain, the number 0·2106: hence the resistance of 240 feet weighing 16½ lb., or 115,500 grains, is

$$0{\cdot}2106 \times \frac{240 \times 240}{115500} = 0{\cdot}105.$$

If the length and weight of the wire whose resistance is required be given in metres and grammes, the calculation must of course be made in the same way, using the number given in the second column of figures. Again, to find the resistance of 10,000 metres of hard-drawn copper wire having a diameter of 2·5 millimetres, we must use the fourth column of figures; in this case the calculation would be

$$0{\cdot}02104 \times \frac{10000}{2{\cdot}5 \times 2{\cdot}5} = 33{\cdot}664.$$

For short ranges of temperature within ordinary limits, the resistance of metallic conductors increases very nearly proportionally to the temperature, and, as Matthiessen has shown (*Phil. Trans.* 1862, p. 23)—with the exception of iron, the resistance of which varies between 0° and 100° C., in the ratio of 1·0 to 1·62—the resistance of the most important metals in a state of purity varies almost exactly at the same rate. The numbers in the last column of the table give the approximate percentage variation

	Resistance at 0° C. of Wires				Approximate percentage variation of resistance, per 1° at 20° C.
	1 foot long weighing 1 grain	1 metre long weighing 1 gramme	1 foot long, 0·001 inch in diameter	1 metre long, 0·001 metre in diameter	
Silver, annealed .	0·2214	0·1544	9·151	0·01937	0·377
„ hard-drawn .	·2421	·1689	9·936	·02103	—
Copper, annealed .	·2064	·1440	9·718	·02057	0·388
„ hard-drawn .	·2106	·1469	9·940	·02104	—
Gold, annealed . .	·5849	·4080	12·52	·02650	0·365
„ hard-drawn .	·5950	·4150	12·74	·02697	—
Aluminium, annealed.	·06822	·05759	17·72	·03751	—
Zinc, pressed . .	·5710	·3983	32·22	·07244	0·365
Platinum, annealed .	3·536	2·464	55·09	·1166	—
Iron, „ .	1·0785	·7522	59·10	·1251	—
Nickel, „ .	1·2425	·8666	75·78	·1604	—
Tin, pressed . .	1·317	·9184	80·36	·1701	0·365
Lead, „ . .	3·236	2·257	119·39	·2527	0·387
Antimony, pressed .	3·324	2·3295	216·0	·4571	0·389
Bismuth, „ .	5·054	3·525	798·0	1·689	0·354
Mercury . . .	18·74	13·071	600·0	1·270	0·072
Platinum-silver alloy (2 : 1) . . .	4·243	2·959	148·35	·3140	0·031
German silver . .	2·652	1·850	127·32	·2695	0·044
Gold-silver alloy (2:1)	2·391	1·668	66·10	·1399	0·065

of resistance for 1° centigrade, for moderate intervals of temperature above or below 20° C. The general effect of changes of temperature between 0° and 100° C. may be expressed, according to Matthiessen's experiments, by the following formula:

$$\rho_t = \rho_0 (1 + at + bt^2),$$

where ρ_t is the resistance of a conductor at the temperature t° C., ρ_0 its resistance at 0°, and a and b are coefficients depending on the material of which it is composed. The following table gives the values of these coefficients for several cases:

	a	b
Pure metals . . .	+ 0·003894	+ 0·00000252
Mercury	+ 0·0007485	− 0·000000398
German silver . . .	+ 0·0004433	+ 0·000000152
Platinum-silver alloy .	+ 0·00031	
Gold-silver alloy . .	+ 0·0006999	− 0·000000062

The following table gives the results of F. Kohlrausch and Nippoldt's experiments (*Pogg. Ann.* cxxxviii. 385) on the resistance of dilute sulphuric acid of various degrees of concentration. The numbers in the third and fourth columns give the resistance and conducting power at 22° C. of a column of acid of given length and section as compared with the resistance and conducting power of a similar column of mercury at 0° C. taken as unity. The last column gives the percentage *increase* of conducting power for a *rise* of temperature of 1° C.:

Resistance and Conducting Power of Sulphuric Acid.

Specific gravity at 18·5° C.	Hydric sulphate per cent.	Specific resistance (Mercury = 1)	Specific conducting power (Mercury = 1)	Percentage variation of conducting power per degree centigrade
1·0504	8·3	34465	0·000029015	0·653
1·0989	14·2	18910	52881	0·646
1·1431	20·2	14962	66837	0·799
1·2045	28·2	13108	76290	1·317
1·2631	35·2	13107	76298	1·259
1·3163	41·5	14259	70130	1·410
1·3597	46·0	15732	63565	1·674
1·3994	50·4	17692	56523	1·582
1·4482	55·2	20756	48182	1·417
1·5026	60·3	25525	39176	1·794

From these determinations, it appears that the mixture of hydric sulphate and water which possesses the greatest conducting power has the sp. gr. 1·233 at 18·5°, and therefore contains 31·5 per cent. of hydric sulphate, and that the conducting power of this acid at 22° is 0·000077274, that of a similar column of mercury at 0° being taken as unity. The last column of the table shows that the variation of conducting power for a change of temperature of 1° is sensibly proportional to the percentage of hydric sulphate in the solution. Calling the percentage variation for 1° δ, and the percentage of hydric sulphate p, the experimental numbers give, when compared by the method of least squares:

$$\delta = 0·4680 + 0·0219\,p.$$

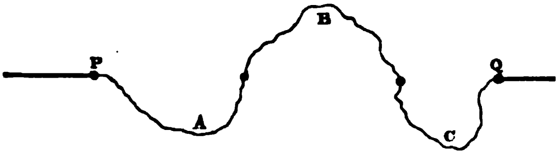
And by help of the coefficient thus calculated, the conducting power k_t at any temperature $t°$ may be deduced from the conducting power k_{22} at 22°, by the formula:

$$k_t = k_{22}\left[1 + \frac{\delta}{100}(t - 22)\right].$$

Resistance of Conductors variously combined.—If any two points, P and Q, are connected together by two or more conductors, A, B, C . . . ., having separately the respective resistances ρ_1, ρ_2, ρ_3 . . . ., and combined together *in series*, as in fig. 23, the resistance r of the whole combination is evidently equal to the sum of the resistances of the separate conductors, or

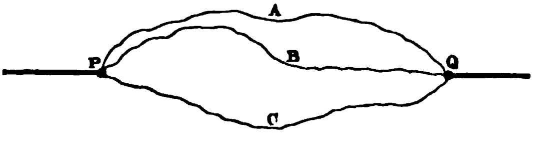
$$r = \rho_1 + \rho_2 + \rho_3 + \ldots$$

FIG. 23.



If, on the other hand, the conductors are connected *in multiple arc*, as in fig. 24, the total resistance between the two given points is represented by

FIG. 24.



$$r' = \frac{\rho_1\rho_2\rho_3}{\rho_2\rho_3 + \rho_1\rho_3 + \rho_1\rho_2}.$$

This relation may be easily proved as follows: Let $\kappa_1, \kappa_2, \kappa_3 \ldots k'$ be the respective conducting powers of the several conductors A, B, C, and of the combination of them represented in fig. 24; then, by the definition of resistance and conducting power, we have:

$$\kappa_1 = \frac{1}{\rho_1} \qquad \kappa_2 = \frac{1}{\rho_2} \qquad \kappa^3 = \frac{1}{\rho_3} \qquad r' = \frac{1}{k'}.$$

Further, it is evident that the conducting power of the combination fig. 24 must be equal to the sum of the conducting powers of the separate conductors, or

$$k' = \kappa_1 + \kappa_2 + \rho_3;$$

whence

$$r' = \frac{1}{\kappa_1 + \kappa_2 + \kappa_3} = \frac{1}{\frac{1}{\rho_1} + \frac{1}{\rho_2} + \frac{1}{\rho_3}} = \frac{\rho_1\rho_2\rho_3}{\rho_2\rho_3 + \rho_1\rho_3 + \rho_1\rho_2}.$$

To find the strength of the current in the several branches of a compound conducting system, such as that indicated in fig. 24, we have to consider that the strength of the current in the undivided part of the circuit is equal to the sum of the currents in the branches, and also that the same electromotive force acts in each of the branch-conductors. The former relation is expressed by the equation

$$C = c_1 + c_2 + c_3 \quad . \quad . \quad . \quad . \quad (1),$$

where C represents the strength of the current in the undivided part of the circuit, and c_1, c_2, and c_3 the currents in the branches A, B, and C respectively. The latter relation gives rise, by Ohm's law, to the equations

$$e = c_1\rho_1 = c_2\rho_2 = c_3\rho_3 \quad . \quad . \quad . \quad . \quad (2),$$

in which e stands for the electromotive force between the points P and Q. Substituting for c_2 and c_3 in (1) their values in terms of c_1 given by (2), we get, for the strength of the current in the conductor A, the value

$$c_1 = C\frac{\rho_2\rho_3}{\rho_2\rho_3 + \rho_1\rho_3 + \rho_1\rho_2};$$

and, by proceeding in a similar way, we obtain the values of c_2 and c_3, namely—

$$c_2 = C\frac{\rho_1\rho_3}{\rho_2\rho_3 + \rho_1\rho_3 + \rho_1\rho_2},$$

and

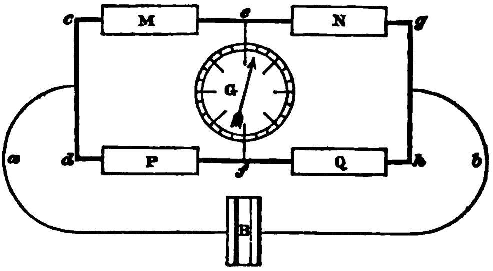
$$c_3 = C\frac{\rho_1\rho_2}{\rho_2\rho_3 + \rho_1\rho_3 + \rho_1\rho_2}.$$

The corresponding expressions for the strength of the current in any one of any number of conductors connecting the same two points is easily obtained from the above, if it is remembered that the numerator in each case is the product of all the resistances *except* that of the branch in question, and that the denominator is the sum of a series of terms formed by multiplying together all the resistances except the first, then all but the second, and so on. A case of very frequent occurrence is a combination of *two* conductors in multiple arc: the expressions for the strength of the currents in the two branches are then

$$c_1 = C\frac{\rho_2}{\rho_1 + \rho_2}, \text{ and } c_2 = C\frac{\rho_1}{\rho_1 + \rho_2}.$$

Method of Comparing Resistances.—The method of measuring the resistance of conductors by comparing them with a rheostat, as described at p. 467, vol. ii., is not capable of giving very accurate results. Of the various more exact methods that have been devised, those which are most generally applicable are modifications of that introduced by Sir Charles Wheatstone in 1843, and known as *Wheatstone's Electrical Bridge or Balance* (*Phil. Trans.* 1843, p. 323). The general principle of this method may be explained by help of the diagram, fig. 25, where B represents a galvanic battery, connected by wires, a and b, with the thick copper conductors cd and gh; G is a delicate galvanometer; and M, N, P, and Q are resistances. One of them, for instance Q, is the resistance to be measured; its neighbour P consists of a rheostat or a graduated set of resistance-coils, so that it can be increased or diminished at will to any required amount; and M and N are adjusted so as to be equal, or to bear some other simple known ratio to each other. M and N are connected by the thick copper conductor e, and P and Q by the similar conductor f, and each of these conductors is connected by a branch-wire with one terminal of the

FIG. 25.



galvanometer. The process of measurement consists simply in altering the value of the resistance P, until, when the battery-circuit is completed, no current passes through the galvanometer, and the needle consequently remains at rest. When this is the case, it can be shown, by the laws of divided currents which have just been stated, that the resistance P is to the resistance Q in the same ratio as the resistance M to the resistance N, and consequently the value of Q is given by the equation:

$$Q = P\frac{N}{M}.$$

To prove this, let C denote the strength of the current in the undivided part, *a* B *b*, of the circuit. The current in *c* M *e* is of the same strength as the current in *e* N *g*, and that in *d* P *f* is equal to that in *f* Q *h*, for, since no current passes through the galvanometer, the currents in *c g* and *d h* are not modified by the presence of the cross connection *e* G *f*. Accordingly, let the strength of the current in *c* M *e* N *g* be denoted by C_1, and the strength of the current in *d* P *f* Q *h* by C_2. Then, since the resistance of the former branch of the circuit may be represented by M + N, and that of the latter by P + Q—the resistances of the connections *c, d, e, f, g, h* being negligible in comparison—we have

$$\frac{C_1}{C_2} = \frac{P + Q}{M + N} \quad \ldots\ldots \text{(a)}.$$

Further, let C_1' represent the part of the current C_1 which would flow from *e* to *f* if the current C_2 did not exist; and let C_2' represent the part of the current C_2 which would flow from *f* to *e* if the current C_1 did not exist; we have then

$$C_1' = C_1 \frac{N}{G + N + Q},$$

and

$$C_2' + C_2 \frac{Q}{G + N + Q}.$$

These currents, C_1' and C_2', would traverse the galvanometer in opposite directions; but, since, in the actual experiment, the galvanometer remains at rest, it is obvious that C_1' and C_2' must be equal to each other, whence

$$C_1N = C_2Q$$

or

$$\frac{C_1}{C_2} = \frac{Q}{N} \quad \ldots\ldots \text{(b)}.$$

Equating the values of $\frac{C_1}{C_2}$ given by equations (a) and (b) and transposing, we get

$$\frac{P + Q}{Q} = \frac{M + N}{N},$$

whence

$$\frac{P}{Q} = \frac{M}{N}, \text{ or } Q = P\frac{N}{M}.$$

(For further details relating to the electrical balance and the mode of using it, see Jenkin, *Brit. Assoc. Rep.* 1862, p. 159; Matthiessen and Hockin, *Brit. Assoc. Rep.* 1864, p. 352; also *The Laboratory*, 1867, pp. 343, 391, 423.)

In certain cases the comparison of resistances by means of the electrical balance requires special precautions or corrections. If, for instance, one of the conductors to be compared consists of alternate pieces of two different metals connected together end to end, as in the thermo-electric pile, the passage of a current through it will cause the points of junction of the metals to be alternately heated and cooled, and will thus generate an electromotive force, opposed to that of the battery, which, in the comparison of resistances, produces the same effect as an increase of resistance. This inverse electromotive force is proportional to the difference of temperature at the alternate metallic joints, and therefore does not acquire a sensible value if the current is allowed to pass for only a very short time; if however the current is maintained, the inverse electromotive force finally attains a constant maximum value proportional to the strength of the current. The effect of this is, as has been shown by Beetz (*Pogg. Ann.* cxxix. 520), equivalent to a constant additional resistance, independent of the strength of the current. Analogous phenomena, causing a complication in the measurement of resistance, arise in the case of electrolytic conductors, in which an inverse electromotive force is caused by the polarisation of the electrodes already described (ii. 429).

In this case also the inverse force gradually increases from zero to a constant maximum when the current is kept up continuously; it is probable therefore that, by employing comparatively large electrodes and currents of very short duration, it would be possible to prevent its producing very serious results. But the only generally applicable method yet devised, by which its effects can be entirely got rid of, consists in the employment of a rapid succession of currents of short duration alternately in opposite directions. By the employment of a process founded upon this principle, F. Kohlrausch and Nippoldt have proved conclusively that, when the disturbing effects of polarisation are got rid of, Ohm's law (ii. 459) applies to electrolytic as fully as to metallic conductors (*Pogg. Ann.* cxxxviii. 280, 370).

Standards of Electrical Resistance. In order that the results obtained by comparing the resistances of various conductors may be comparable among themselves, it is needful that one term of the comparison should either be identically the same in every case, or else that it should bear a known relation to some one invariable standard. Accordingly, various propositions have been made from time to time with a view to induce different experimenters to use the same standard or *unit* of resistance, and so to make the results of their experiments mutually comparable. Hitherto, however, no one standard has come to be universally employed; and the comparison of measurements made by reference to the different units which are in partial use presents difficulties of the same kind as, but greater in degree than, the comparison of measurements of length or mass expressed in terms of the standards employed in different countries. The following table gives the approximate relative values of the standards of electrical resistance most commonly referred to in scientific writings:

Standards of Resistance.

Name of Standard	Definition	Relative Values		
		B. A. unit, or Ohmad	Weber's unit $\times 10^{10}$	Mercury unit
British Association unit, or Ohmad	10^7 metres per second, according to experiments of British Association Committee	1	0·9297[a]	0·9536[b] 0·9619[c]
Weber's unit $\times 10^{10}$	10^7 metres per second, according to Weber's experiments	1·0756[a]	1	1·0257[e]
Mercury unit according to Siemens Matthiessen	Column of mercury 1 metre long, 1 sq. millim. in section	1·0486[b] 1·0396[c]	0·9749[e]	1
Jacobi's unit	25 feet of a particular copper wire	1·586[d]	1·672[f] 1·474[g]	1·512[h]

[*Authorities.*—[a] Calculated from [b] and [e]. [b] Siemens, *Pogg. Ann.* cxxvii. 342; *Fortschritte der Physik*, xxii. 372. [c] Matthiessen, *Brit. Assoc. Rep.* 1864, p. 349. [d] Calculated from [b] and [h]. [e] Weber, 'Galvanometrie,' *Fortschritte der Physik*, xviii. 427. [f] Weber, *Elektrodynamische Maassbestimmungen*, 2te Abhandl. p. 252. [g] Calculated from [e] and [h]. [h] Calculated by Wiedemann (*Galvanismus*, ii. 915) from Siemens's experiments, *Pogg. Ann.* cx. 9 and 13.]

In this table, the numbers in each vertical column express the resistance of the standard named at the head of it in terms of the other standards, while the numbers in each horizontal line give the relative resistances of the several standards. These numbers, however, cannot lay claim to any high degree of accuracy, as exact intercomparisons of the various units are wanting. The nature of the units adopted by Weber and by the Committee of the British Association, and the meaning of the definitions of them given in the table, will become more apparent from what follows.

If electrical resistance were an independent magnitude, it would be, comparatively speaking, a matter of indifference what unit was adopted for measuring it, so long as the unit itself had an accurately defined value; but, seeing that electrical resistance can only be defined by reference to the correlative magnitudes *electromotive force* and *electric current*, it is obviously desirable that the units adopted for the measurement of resistance, electromotive force, and electric current should be chosen so as to express the mutual relations of these magnitudes in the simplest and most direct way possible. When the same electromotive force acts in circuits of various lengths, or composed of various materials, it produces in general electric currents having different degrees of strength; and the 'resistance' of each circuit is simply the name given to that quality of it which determines the strength of the current produced by a given electromotive force. According to Ohm's law, the resistance R of a circuit in which the electromotive force E produces the current C is expressed by the formula

$$R = a\frac{E}{C},$$

where a is an arbitrary constant depending upon the units of measurement adopted for R, E, and C. The physical meaning of a becomes apparent if we suppose that E and C each $= 1$: the above expression then becomes

$$R = a,$$

which shows that a is (1) the resistance of a circuit in which unit electromotive force would produce a current of unit strength. Again, if we make $E = R = 1$, we get $C = a$; or, by making $C = R = 1$, we find $\frac{1}{E} = a$; whence we see that a may also be defined (2) as the strength of the current produced by unit electromotive force in a circuit of unit resistance, or (3) as the reciprocal of the electromotive force required to produce the unit current in a circuit of unit resistance. Now it is obvious from these relations, that whatever be the units adopted for measuring two of the magnitudes R, E, and C, it is always possible to choose such a unit for the measurement of the third as will make the coefficient $a = 1$. In this case the formulæ expressing Ohm's law assume their simplest possible form, namely,

$$R = \frac{E}{C}, \quad C = \frac{E}{R}, \quad E = CR,$$

and the unit of resistance would then be defined as *the resistance of a circuit in which unit electromotive force produces the current of unit strength.* Ohm's law then determines the relation which the units of resistance, current, and electromotive force must bear to each other in order that they may form a coherent system; but it leaves us free to choose any two of them quite arbitrarily.

A further condition, however, which a satisfactory system of electrical measures must fulfil, is that of expressing conveniently the relations of electrical to other physical magnitudes. The most fundamental of these relations are determined by Joule's discoveries of the laws according to which mechanical energy and the energy of current electricity are respectively converted into heat. These laws are expressed by the equations

$$W = JH$$

and

$$H = b.C^2Rt,$$

where J stands for the mechanical equivalent of heat, W for the number of units of work which must be expended to produce the same quantity of heat, H, as would be produced in the time t by a current of the strength C in a conductor of the resistance R, and b for a constant depending on the units of measurement for heat, current, and resistance. Combining the two equations, we get

$$W = Jb.C^2Rt = Jb.ECt = Jb\frac{E^2}{R}t.$$

If we suppose C to denote a current of unit strength, R a unit of resistance, and t a unit of time, the value of W becomes

$$W = Jb.$$

But, in a natural system of measures, the unit current circulating for unit of time in a conductor of unit resistance would perform unit of work or its equivalent. In order that this condition may be fulfilled, the units adopted for the measurement of work and for the electrical magnitudes E, C, and R must be so chosen as to make the factor $Jb = 1$. We then get, for the work done by an electric current in unit of time, the expressions

$$W = C^2R = EC = \frac{E^2}{R},$$

establishing a relation between the unit of work and the electrical units. But the unit of work is defined, independently of electrical phenomena, as the work done by the unit force when it acts through unit of distance; and the unit force is itself defined as the force required to impart unit velocity to unit mass in the unit of time; consequently, the measurement of work involves reference only to the fundamental physical units of space, time, and mass. If then we can define either the unit of electromotive force, of current, or of resistance, without reference to anything beyond the same fundamental units, two of the four magnitudes occurring in the above equations are determined, and the equations themselves suffice for determining the other two. Now the phenomena of the mutual action of electric currents and magnets afford the means of measuring both electric currents and electromotive force in terms of the units of space, time, and mass, and therefore of obtaining an independent definition of the natural unit of each. From the units thus determined, the unit of resistance can be deduced by Ohm's law. Hence a system of electrical measures can be based, either upon the phenomena of electromagnetism alone, or upon these phenomena taken in connection with the laws of the production of work by electric currents; and if the experimental data required in each case were perfectly accurate, the measures obtained by the two methods would be identical. Hitherto, however, it is probable that the measures derived solely from electromagnetic phenomena are the most trustworthy, and it is upon them that both Weber's unit of resistance and the British Association unit are founded. By definition, these two units would be identical (except that, as a matter of practical convenience, the B. A. unit is taken 10,000,000,000 times as great as Weber's), were it not for experimental errors.

Standards of measure which, like those we have been discussing, are derived from the units of space, time, and mass, are often called *absolute* standards, not as implying any special accuracy in the measurements made by means of them, but in contradistinction to *comparative* measures, which merely enable us to express the relation between the magnitude to be measured and some other magnitude of its own kind. Thus, the cubic foot, or the cubic inch, may be called an absolute unit of capacity, while the gallon, or the pint, is merely a relative unit.

We shall now try to explain the general principles of the methods by which electric currents, electromotive force, and resistance can be measured in absolute units.

Absolute Measurement of Electric Currents.—The force exerted by an element of the length s of a current of the strength C upon a magnetic pole of intensity M, at a distance r in a direction making an angle θ with the tangent to the current at the position of the element in question, is directly proportional to the length of the element of the current, to the strength of the current, to the intensity of the magnetic pole, and to the sine of the angle θ, and inversely proportional to the square of the distance; and its direction is perpendicular to the plane passing through the element of the current and the pole. The force may therefore be represented in magnitude by the formula

$$f = \frac{sCM \sin \theta}{r^2}.$$

If the current is carried round the circumference of a circle with the magnetic pole at the centre, each element of it is at the same distance from the pole, and $\sin \theta$ is throughout equal to unity, and the plane containing the whole current also contains the pole; hence the resultant force F exerted by the entire current is the product of the force f exerted by each element into the number of elements $\frac{2\pi r}{s}$ in the whole circumference, or

$$F = \frac{2\pi CM}{r}.$$

If, instead of a single magnetic pole at the centre of the circle round which the current passes, there is a complete magnet with poles of the intensity M and $-M$.

but with the distance between them, L, so short, in comparison to the radius of the circle, that each pole may, without sensible error, be regarded as at the centre, the two poles are subject to equal parallel forces in opposite directions; and the perpendicular distance between the lines of action of these forces is L cos a, if a be the angle which the axis of the magnet makes with the plane of the current. Consequently, the magnet is subject to a statical couple, tending to set its axis perpendicular to the plane of the current, the moment of which is

$$G = FL \cos a = \frac{2\pi C\mu}{r} \cos a,$$

where $\mu = ML$ stands for the magnetic moment of the magnet. If the plane of the current be vertical and coincide with the plane of the magnetic meridian, the magnet is also subject to a couple, tending to set its axis parallel to the plane of the current, of which the moment is

$$E = H\mu \sin a,$$

where H is the horizontal component of the earth's magnetic force. The magnet therefore, under the action of these two opposing couples, comes to rest in such a position that their moments are equal, that is so as to make

$$\frac{2\pi C\mu}{r} \cos a = H\mu \sin a.$$

This equation gives, for the strength of the current in terms of the radius of the circle, the deflection of the magnet from the meridian, and the horizontal component of the earth's force, the expression

$$C = \frac{Hr}{2\pi} \tan a.$$

The conditions that have been supposed in deducing this formula are approximately fulfilled in the simplest form of tangent-galvanometer (ii. 460); the observation of the deflection which a given current produces on a tangent-galvanometer of known radius affords a measure of the strength of the current in absolute units, when the horizontal component of the earth's magnetic force, at the time and place of the experiment, is known in absolute measure. (See iii. 781, 782; also MAGNETISM in this Supplement.) The definition of the unit current which results from this mode of measurement is as follows:

A current of unit strength is a current of which the unit length placed along the circumference of a circle of unit radius (the current therefore occupying an arc of 57°·29578), *the plane of which is parallel to the lines of force of a magnetic field of unit intensity, would cause a short magnet suspended at the centre of the circle to be deflected through an angle* (= 45°) *whose tangent is unity.*

Or the same definition may be put into a form in which it is more directly applicable to the tangent-galvanometer, thus:

A current of unit strength placed once round the circumference of a circle of unit radius, in the plane of the magnetic meridian, will cause a short magnet suspended at the centre of the circle to be deflected through an angle whose tangent is 6·2832 ($= 2\pi$) *divided by the absolute horizontal intensity of the earth's magnetic force at the time and place of observation.*

It will be seen that, in order to determine the strength of a current in absolute measure, by means of the tangent-galvanometer, the absolute intensity of the earth's horizontal magnetic force must have been ascertained by independent observations. But if the current be made to traverse a coil of wire, suspended so that its axis is horizontal and perpendicular to the magnetic meridian when no current is passing, as well as a tangent-galvanometer, the observation of the deflection of the coil combined with that of the tangent-galvanometer gives, as has been shown by Kohlrausch, the data for determining simultaneously the absolute horizontal force of the earth and the absolute strength of the current. The general principle of this method may be stated as follows: When a current of the strength C traverses the coil, it develops a statical couple tending to set the axis of the coil parallel to the magnetic meridian, the moment of which is obtained by multiplying the strength of the current by the horizontal magnetic force of the earth H, by the total area A enclosed by the coil (that is, the mean area enclosed by a single turn of the wire multiplied by the number of turns), and by the sine of the angle β which the axis of the coil makes with the magnetic meridian; but the coil is also subject to another couple, tending to set its axis perpendicular to the meridian, the moment of which is the coefficient of torsion-elasticity of

the suspending wires T, multiplied by the angle of deflection of the coil. Hence the position of equilibrium of the coil, when the current is passing, is determined by the equation

$$\mathrm{CH.A}\sin\beta = \mathrm{T}\,(90^\circ-\beta)$$

or

$$\mathrm{CH} = \frac{\mathrm{T}\,(90^\circ-\beta)}{\mathrm{A}.\sin\beta} \; \ldots\ldots \; (a).$$

And the simultaneous observation with the tangent-galvanometer gives

$$\frac{\mathrm{C}}{\mathrm{H}} = \frac{r}{2\pi}\tan\alpha \; \ldots\ldots \; (b).$$

The combination of these two equations, (*a*) and (*b*), gives both C and H in absolute measure. (For further details, see F. Kohlrausch, *Pogg. Ann.* [1869] cxxxviii. 1.)

Absolute Measurement of Electromotive Force.—The electromotive force of a galvanic battery, or other equivalent apparatus, may be defined as the quality in virtue of which it tends to do work by the transference of electricity from one point to another; and it may be expressed numerically by the amount of work done during the transfer of the unit quantity of electricity. Thus if W be the work done by the chemical or other forces of the battery, during the transfer of the quantity of electricity Q through the circuit, the electromotive force of the battery may be represented by

$$\mathrm{E} = \frac{\mathrm{W}}{\mathrm{Q}} = \frac{\mathrm{W}}{\mathrm{C}t},$$

the last expression being applicable when the electricity is transferred in the form of a current of uniform strength C lasting for the time t. Hence the electromotive force of a battery may also be said to be the work done when a current of unit strength is maintained for unit of time. The work may of course be of various kinds, as, for example, production of heat; work against gravity, as when weights are raised by an electromagnetic engine; work of acceleration against inertia; chemical work, as in a voltameter; magnetic and electrical work, as in an induction coil; but in the above formula it is supposed to be always expressed in absolute mechanical units.

But, just as electromotive force does work in a conducting circuit through the agency of the current which it produces, so, conversely, work done upon a conductor may give rise to electromotive force, and therefore to a current, if the conductor forms part of a closed circuit. This fact, coupled with the condition that the electromotive force developed when unit of work is expended per unit of time is to be taken as the unit of electromotive force, serves as the basis for the absolute measurement of electromotive force. The principles of the measurement will be easily understood from the following considerations.

If a current of the strength C′ circulate in a rectilinear conductor of length l placed at right angles to the lines of force in a uniform magnetic field of intensity H, every element dl of the current is subject to a force equal to

$$\mathrm{HC}'dl$$

in a direction perpendicular to the current and to the lines of force. The resultant force acting upon the whole length l is therefore the sum of the forces acting upon the several elements of it, or

$$\mathrm{F} = \mathrm{HC}'l;$$

and if the conductor be displaced through the distance D perpendicularly to itself and to the lines of force, and in opposition to the force F, a quantity of work w will have been expended in producing the displacement which is expressed by

$$w = \mathrm{FD} = \mathrm{HC}'l\mathrm{D},$$

or, if the displacement take place with the constant velocity v and occupy unit of time, we may write

$$w = \mathrm{HC}'lv.$$

If E be the electromotive force acting in the conductor when at rest, the work (in thi case simply evolution of heat) done in unit of time by the electrical forces when the strength of the current is C′, will be

$$\mathrm{W} = \mathrm{EC}'.$$

But the principle of the Conservation of Energy requires that, when an amount of work w is done upon the conductor by external forces, the equivalent of this work shall make its appearance in the conductor: hence, during the displacement, for the whole quantity of work developed in the conductor per unit of time we have

$$W' = W + w.$$

But in order that a quantity of work W′ may be done in a conductor in a unit of time by a current of strength C′, the electromotive force must be E′, such that

$$W' = E'C'.$$

And this expression, taken in connection with the last three, gives

$$E' = E + Hlv.$$

Hence we see that by displacing the conductor in opposition to the electromagnetic forces, the electromotive force acting in it has been increased by an amount H*lv*; or, in other words, that the movement of the conductor has developed an additional electromotive force proportional to the length of the conductor, the intensity of the magnetic field, and the velocity of the motion. And in order that the relation between the expenditure of work and production of electrical effects may be expressed in the simplest way possible, the electromotive force developed under conditions such as we have been considering must be measured numerically by the product H*lv*, which is equivalent to adopting as the unit of electromotive force *the electromotive force developed when a rectilinear conductor of unit length is moved with unit velocity at right angles to its own length and to the lines of force of a magnetic field of unit intensity.*

Although the preceding considerations suffice to afford a perfectly definite conception of the mechanical unit of electromotive force, it would be exceedingly difficult, in practice, so to arrange matters as to cause electromotive force to be continuously developed under the precise conditions which, for the sake of simplicity, we have taken as the basis of the above discussion. But the principle would remain exactly the same if, instead of a conductor of which every point moved with the same velocity, we had one of which the different points moved with different velocities, and if, instead of moving at right angles to the lines of magnetic force, the conductor cut them at any angle. In such a case, however, instead of being able to represent the electromotive force due to the movement by the simple formula

$$e = Hlv,$$

where v is the velocity of displacement of any point of the conductor, it would be represented by

$$e = H\lambda u,$$

where λ stands for the length of the projection of the straight lines joining the ends of the conductor upon a plane perpendicular to the lines of force, and u for the mean velocity of displacement of this projection perpendicularly to itself and to the lines of force.

The conditions here supposed are most easily realised practically by means of a circular metallic disc rotating in its own plane about an axis through its centre. An electromotive force is developed, due to the movement across the direction of the earth's magnetic force of the several radii of the disc; and if one terminal of a galvanometer be connected with a metal spring pressing against the edge of the disc, and the other terminal be connected with the centre, the galvanometer will indicate the passage of a current as long as the rotation of the disc continues (Faraday, *Experimental Researches*, vol. i. pp. 44, 45; Series ii. par. 149–152). In this case, the conductor by whose movement the current is produced is the radius of the disc which at any instant completes the galvanometer circuit; and, since in the case of a straight line rotating about one end the average velocity of the whole line is the same as that of its middle point, it is easy to see that, if r be the radius of the disc, ω its angular velocity (or the velocity of a point at unit distance from the centre), H the absolute magnetic force of the earth at the time and place of the experiment, and α the angle between the axis of rotation and the direction of the earth's force, the electromotive force causing the current through the galvanometer may be represented by

$$e = H\frac{r}{2}\omega\cos\alpha.$$

Hence the arrangement that has been indicated affords one means of developing an electromotive force which can be measured in absolute units, under conditions in which it can produce a continuous current; and, consequently, all that we require further in order to be able to measure electromotive forces, produced in any way whatever, in absolute units, is a method of comparing one electromotive force with another. But before discussing the processes for the comparative measurement of electromotive forces, it will be most convenient to discuss the principles involved in the absolute measurement of electric resistance.

Absolute Measurement of Electric Resistance. We have already seen that the strength of electric currents and the intensity of electromotive forces can be expressed in terms of the fundamental mechanical units. Consequently, if we express thus the intensity of the electromotive force acting in a given circuit, and also the strength of the current produced by it, the ratio of the numbers expressing these magnitudes will express similarly the absolute *resistance* of the circuit. In this way the absolute resistance of a particular conductor may be ascertained, and from this the absolute resistances of other conductors can be deduced by comparative methods. For the purpose of accurate measurements, the current produced by a revolving disc, as in the experiment above described, could not be satisfactorily employed, as it is practically impossible to keep the resistance at the point of contact between the moving edge of the disc and the spring connected with the galvanometer constant; but the principle that has been indicated has been put in practice in various ways by W. Weber (*Elektrodynamische Maassbestimmungen*, 2te Abhandlung [1850]. *Zur Galvanometrie* [1862]; in abstract, *Fortschr. d. Phys.* xviii. 417), and by Maxwell, Stewart, Jenkin, and Hockin, acting as a sub-committee of the British Association for the Advancement of Science (*Rep. Brit. Assoc.* 1863, p. 163; *ibid.* 1864, p. 350). Two methods were employed by Weber, the general nature of which may be described as follows: In the first, a momentary current was produced by causing a flat annular coil of insulated wire to make rapidly a half-turn about either its horizontal or its vertical diameter, and the strength of the current was deduced from the throw of a magnetic needle, suspended either inside the movable coil itself, or within a galvanometer coil which made part of the same circuit with the movable coil. The electromotive force was in this case known from the dimensions of the coil, the rapidity of its motion, and the absolute intensity of the earth's magnetic force. In Weber's second method, a magnetic needle suspended inside a galvanometer-coil, the terminals of which were connected together, was displaced from the magnetic meridian and then left to itself, and the amplitude of the gradually diminishing oscillations about its position of equilibrium was observed for a considerable number of oscillations. In this experiment, an electromotive force was produced, the intensity of which depended upon the magnetic moment of the magnet, the velocity of its motion, and the dimensions of the coil; and this caused a current in the coil, always in such a direction as to oppose the motion possessed by the magnet at any given instant, the strength of which was indicated by the rate at which the amplitude of the oscillations of the magnet diminished (allowance being of course made for the retarding effect of the air and the viscosity of the suspending fibre). The method employed by the sub-committee of the British Association consisted in causing the coil of a tangent-galvanometer of known dimensions to revolve at a known speed about its vertical diameter, and in observing the deflection of the galvanometer-needle caused by the currents induced in the revolving coil by the earth's magnetism. In these experiments, the tangent of the angle of deflection was directly proportional to the strength of the induced current, and inversely proportional to the horizontal component of the earth's magnetic force. The strength of the current however was directly proportional to the earth's horizonal magnetic force, and depended also upon the velocity of rotation and the resistance of the coil. Hence the tangent of the deflection was both directly and inversely proportional to the earth's horizontal magnetic force, or, in other words, was independent of this force altogether, and therefore the only data required for determining the resistance of the coil, in addition to the number of convolutions of the wire and its mean distance from the magnet, were the velocity of revolution of the coil and the deflection of the magnet.

All these processes, being dependent upon the fundamental relation expressed by the equation,

$$R = \frac{E}{C},$$

give the value of R expressed in the same terms as those adopted for the measurement of E and C. But, as we have seen (p. 571), the absolute strength of a current may be expressed in electro-magnetic measure by the formula

$$C = Hr\frac{\tan a}{2\pi},$$

in which r stands for a length, and the factor written in the form of a fraction is a pure number. Further (p. 573), electromotive force is expressed in absolute electromagnetic measure by the formula

$$E = Hlv,$$

where l again represents a length. Consequently, it follows that the resistance of any conductor, or the quotient of the electromotive force acting in it by the strength of the current produced, must be expressed by a velocity. *The absolute unit of resistance is therefore identical with the unit of velocity*; and this same result would be arrived at, whatever were the experimental process adopted for the actual measurement of electromotive force and current-strength. In all cases it will be found that the expression for electromotive force, if written out in terms of its ultimate physical factors, the units of space, time, and mass, represents the square root of a force multiplied by a velocity; and that the expression for the strength of a current represents the square root of a force, and therefore that their quotient represents a velocity.

Hence the magnitude of the absolute unit of resistance depends only upon the magnitudes of the units of length and time, and Weber, adopting 1 millimetre as the unit of length and 1 second as the unit of time, necessarily defined the absolute unit of resistance as a velocity of 1 *millimetre per second.* This however represents a resistance so very much smaller than those which have most frequently to be dealt with in practice, that the adoption of Weber's unit would lead to inconveniently high numbers for expressing ordinary resistances; consequently, as a matter of practical convenience, the Committee of the British Association upon Electrical Standards (see *Rep. Brit. Assoc.* 1862, p. 125) adopted a unit which, by definition, represents a resistance ten thousand million times as great as Weber's, namely a velocity of 10 *million metres per second.* This standard is variously referred to as the '$\frac{10^7 \times \text{metre}}{\text{second}}$ unit,' the 'B. A. unit,' or the 'Ohmad.'

The absolute unit of resistance may also be deduced from the relation expressed by the equation

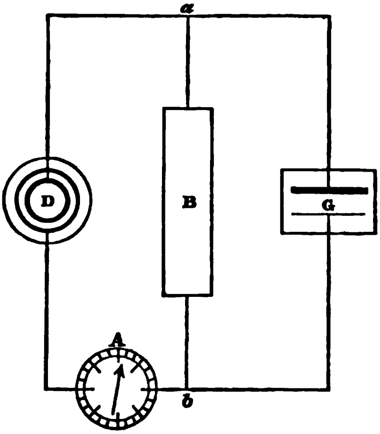
$$R = \frac{W}{C^2 t},$$

where W represents the work done in the time t by a current of the strength C in a conductor of resistance R. The numerator of this expression represents a force multiplied by a length, and the denominator represents a force multiplied by a time (since C is equivalent to the square root of a force); hence we find here again that resistance is measured by the ratio of a length to a time, that is, by a velocity. Determinations upon the principle here indicated have been made by H. Weber (*Fortschr. d. Phys.* 1863, xix. 417). The strength of the current employed was measured by a tangent-galvanometer, and the work done by it in the conductor was calculated from the quantity of heat evolved. Experiments of a similar kind have also been made by Joule (*Rep. Brit. Assoc.* 1867, p. 512), but with a converse purpose; Joule's object having been to deduce the value of the mechanical equivalent of heat, from the quantity of heat developed in a given time, by a current of known strength, in a conductor of which the absolute resistance was known from independent experiments.

[For a further account of the British Association unit of resistance, and a comparison of the various units that are or have been in use, see Fleeming Jenkin, *Proc. Roy. Soc.* (1865) xiv. 154; *Phil. Mag.* [4] xxix. 477].

Comparison of Electromotive Forces. The method given at p. 465 of vol. ii. is not capable of giving trustworthy results in the case of batteries whose electromotive force varies with the strength of the current which passes through them, as is the case, for example, with a battery of Smee's construction, and with most other batteries containing only a single liquid. Such batteries have a definite electromotive force only when the current has a determinate value, and the only condition in which we can be sure that two or more are truly comparable is when they are not traversed by any current at all. This condition may be realised, either by interposing an infinite resistance between the poles (that is, by leaving them disconnected), or by balancing their electromotive force by an equal and opposite force. In the former case the measurement of electromotive force comes to be simply a measurement of the difference of statical tension upon the poles, and may be effected by means of a Thomson's electrometer (p. 553). Several methods, founded upon the second general principle mentioned above, have been devised; but they may all of them be regarded as modifications of one which was introduced many years ago by Poggendorff (*Pogg. Ann.* liv. 161 [1841]), and is known as his *method of compensation*. The general nature of this method will be understood from the following description. Let D and G (fig. 26) represent the two cells whose electromotive forces are to be compared, the electromotive force of G being greater than that of D (for instance, G being a Grove's, and D a Daniell's cell). The cells are to be united, by wires connecting their similar poles, so as to form parts of the same circuit, at some part of which a galvanometer A is to be inserted. Then a point *a*, in the conductor which connects one pole of D with the like pole of G, is to be connected, by a conductor *a* B *b*, of known resistance which can be varied at pleasure (such as a rheostat or set of resistance-coils), with a point *b* in the conductor which connects the galvanometer with the other pole of G; and, lastly, the resistance at B is to be increased or diminished until no current circulates in the branch *a* D A *b*, and consequently the galvanometer A shows no deflection. Calling E_D and E_G the electromotive forces of the two cells, and R and R_G the resistances of the branches *a* B *b* and *a* G *b* respectively, we have for the ratio of the electromotive forces:

FIG. 26.



$$\frac{E_D}{E_G} = \frac{R}{R + R_G}.$$

This formula is easily established from the following considerations. Since there is no current in the part of the circuit containing the cell D and the galvanometer, the strength of the current in G and the condition in all respects of the circuit G *a* B *b* G would be unchanged if the branch *a* D A *b* were removed. Then, putting C for the strength of the current in G, we have

$$E_G = C(R + R_G);$$

and, since the strength of the current through B is the same as that through G, we have also

$$E = CR,$$

if E represents the electromotive force acting between *a* and *b*. Hence

$$\frac{E}{E_G} = \frac{R}{R + R_G}$$

But, since there is no current through D and A, the electromotive force between *a* and *b* must be equal to that of the cell D, and must tend to produce a current through D in the opposite direction to that which the electromotive force of this cell would produce if it acted alone in the circuit. That is

$$E = E_D \quad \text{or} \quad \frac{E_D}{E_G} = \frac{R}{R + R_G}.$$

The same relation is also easily deduced from the principles discussed at p. 565, as applying to the strength of currents in divided circuits. It is only needful to write down the strength of the current in the branch a D A b due to the cell D, and the strength of the current in the same branch due to the cell G, and to make their sum = 0, in order to arrive at the above equation.

It will be seen that this method gives the ratio of the electromotive forces to be compared in terms of the resistances R and R_G. Of these, R, which is the resistance of a metallic conductor, can always be ascertained within a very small fraction of its whole amount; but R_G, which includes the resistance of the cell G, cannot in general be measured with equal accuracy. If, however, a great metallic resistance—say 2,000 or 3,000 units—be introduced into the branch a G b, any uncertainty in the determination of the resistance of G becomes of small consequence in comparison with the total resistance R_G, and indeed, in such a case, the resistance of the cell may be generally entirely disregarded. Even if it is inconvenient to introduce into the branch a G b a metallic resistance so great that the resistance of the cell is negligible in comparison, the necessity of knowing what the resistance of the cell is may be avoided by the following artifice, due to Bosscha (*Pogg. Ann.* xciv. 172 [1855]). The connections are made exactly in the way that has been described, and the resistance at B is adjusted so as to cause no current to traverse the galvanometer A. Then the resistance R_G is increased or diminished by a known amount r_G, whereby a current is produced either in one direction or the other through A, and lastly the resistance at B is increased or diminished so as again to destroy the current in A: let r be the alteration required for this purpose; then the first experiment gives, as before,

$$\frac{E_D}{E_G} = \frac{R}{R + R_G},$$

and the second experiment gives

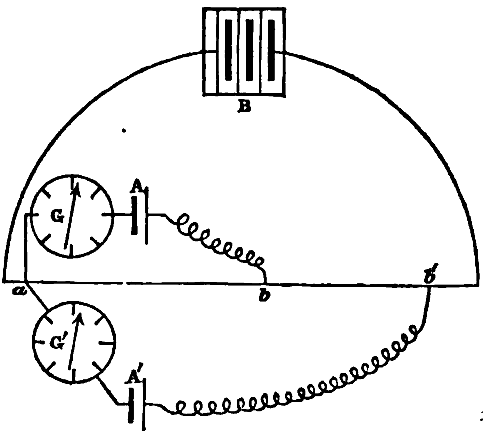
$$\frac{E_D}{E_G} = \frac{R + r}{(R + r) + (R_G + r_G)};$$

and therefore, from the two together we get

$$\frac{E_D}{E_G} + \frac{r}{r + r_G}.$$

Another modification of Poggendorff's method, which presents the advantage of making the conditions of the two cells to be compared exactly similar, by simply allowing neither of them to be traversed by a current, has been devised by Mr. Latimer Clark (*Elementary Treatise on Electrical Measurement* [London, 1868] p. 106). In this method, the poles of a battery of considerably greater electromotive force than either of the cells to be compared are connected by a metallic conductor of great resistance; the similar poles of both the cells to be tested, the positive poles for instance, are then connected with the same point of this conductor, and the points are found by trial with which the other pole of each cell must be connected in order that neither of them may be traversed by a current. The above diagram (fig. 27), in which A and A'

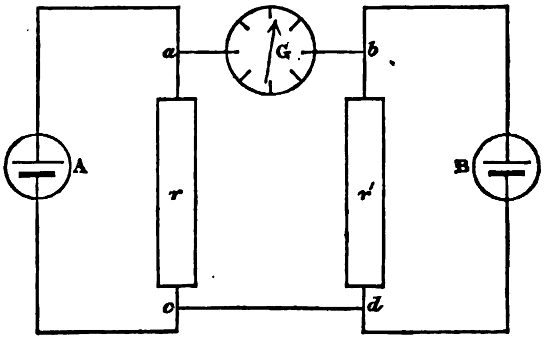
FIG. 27.



denote the cells to be compared, B a battery of greater electromotive force, and G and G′ galvanometers which show whether or not any current is passing through A or A′, will help to explain the mode of arranging the apparatus. It is plain that, when the indicated connections have been made, and both the galvanometers remain at zero, the electromotive force of the cell A is to that of the cell A′ in the same ratio as the resistance of the portion of the conductor of the battery B included between the points *a* and *b* is to that of the portion included between the points *a* and *b′*. A special apparatus constructed by Mr. Clark for conveniently measuring electromotive forces by this method will be found described in the work referred to above.

Another simple modification of Poggendorff's arrangement enables us to ascertain whether the electromotive force of a cell when producing a current varies with the resistance of the circuit, and if so to what extent. This will be readily understood from the following diagram (fig. 28), where A and B represent, one of them a standard cell,

Fig. 28.



and the other a cell to be compared with it, and G a galvanometer one terminal of which is connected with the point *a* in the circuit of the cell A, and the other with the point *b* in the circuit of the cell B. Then, if the points *c* and *d* are also connected by a conductor, and the resistances in the various parts of the two circuits are so adjusted that no current traverses the galvanometer, it will be easily seen that the electromotive force acting between the points *a* and *c* must be equal to that acting between the points *b* and *d*; and since the former is the same fraction of the total electromotive force of the cell A that the resistance between *a* and *c* is of the resistance of its whole circuit, and the latter is to the total electromotive force of the cell B as the resistance between *b* and *d* is to the whole resistance of this circuit, we get for the ratio of the electromotive forces of the two cells the expression

$$\frac{E}{E'} = \frac{Rr'}{Rr},$$

in which E stands for the electromotive force of the cell A, R for the total resistance of the circuit A *a c* A, and *r* for the resistance between *a* and *c*, while E′, R′, and *r′* denote the corresponding magnitudes in the case of the cell B.

The electromotive force of cells of professedly the same construction is not always identical, but varies within small limits in consequence of causes which have not been thoroughly investigated, but of which the most important are probably the greater or less purity of the metals and solutions employed, and the degree of concentration of the latter. The following table gives the average electromotive forces of several of the best known cells compared with that of a Daniell's cell taken as unity:

Electromotive Forces of Galvanic Cells.

Construction of Cell	Electromotive Force	Authority
Daniell's	1	
Grove's	1·67 to 1·81	Poggendorff.
„	1·75	Buff.
„	1·79	Latimer Clark.
Bunsen's	1·75	L. Clark; J. Müller.
„	1·70 to 1·87	Buff.
Smee's (when not in action) .	1·02	Clark.
„ „	1·05	Poggendorff.
„ (when in action) .	about 0·45	Clark.
„ „ .	0·65	Joule.
„ „ .	0·44	Bosscha (by calculation).
Copper and zinc in dilute sulphuric acid . . .	0·82	Poggendorff; Clark.
Chloride of silver and zinc in solution of sodium chloride (25 grms. to 1 litre water)	1·0	De la Rue and H. Müller. Paalzow.
„ „ „ „ .	1·11	Clark.
Zinc in dilute sulphuric acid, graphite in solution of 1 pt. potassium bichromate, and $1\frac{1}{3}$ pt. hydrogen sulphate in 6 pts. water	1·57	Poggendorff.
Zinc in dilute sulphuric acid, graphite in solution of 1 pt. potassium bichromate, and $2\frac{1}{12}$ pts. hydrogen sulphate in $8\frac{1}{3}$ pts. water	1·97	Buff.
Zinc in dilute sulphuric acid, carbon in mercurous sulphate (Marié-Davy) . .	1·26 1·21	J. Regnauld. Clark.
Zinc and binoxide of manganese in saturated solution of ammonium chloride (Leclanché)	1·382 0·896	Leclanché. Müller.

The absolute electromotive force of a Daniell's cell is estimated by Bosscha at 10·258, by Thomson at 10·79, and by von Waltenhofen (*Pogg. Ann.* cxxxiii. 478) at 10·8; that is to say, a Daniell's cell would produce, in a circuit whose total resistance was 1 B. A. unit, a current of a little more than *ten* times the unit current as defined at p. 571.

The following determinations are given by Kohlrausch (*Pogg. Ann.* cxli. 456): they are expressed in terms of Siemens's mercury-unit of resistance and of the absolute unit of current:

Electromotive force of a Grove's cell (platinum, concentrated nitric acid, sulphuric acid of sp. gr. 1·06, freshly amalgamated zinc) = 19·98.

Electromotive force of a Daniell's cell (copper, saturated solution of cupric sulphate, sulphuric acid, and zinc, as above) = 11·71.

Electromotive force of a cell formed of copper, sulphuric acid, and zinc (as above) = 10·82.

Electromotive forces of thermo-electric couples, one joint being at about 16° C., and the other $t°$ higher:

1. German-silver and copper—

$$e = 0·0001549t + 0·000000291t^2.$$

2. Copper and iron—

$$e = 0·0000969t - 0·000000149t^2.$$

3. German-silver and iron—

$$e = 0·0002476t + 0·000000196t^2.$$

[A very instructive exposition of the general relations of electrical magnitudes, by Profs. J. Clerk Maxwell and F. Jenkin, will be found in Appendix C to the second Report of the Committee of the British Association on Standards of Electrical Resistance (*Brit. Assoc. Rep.* 1863, p. 130); and a clear and concise statement of the general principles of the most important electrical measurements has been given by M. Bertin in the *Annales de Chimie et de Physique* for December 1869 and April 1870 (vol. xviii. pp. 446–461; vol. xix. pp. 483–501).] G. C. F.

ELIC ACID. An acid existing, according to Chevreul (*Compt. rend.* lxii. 1015), in the sweat of sheeps' wool. It is a colourless liquid, somewhat heavier than water, nearly insoluble therein, but soluble, with acid reaction, in alcohol and ether. The barium salt, which is likewise soluble in alcohol, decomposes in dilute aqueous solution, with separation of a varnish-like acid salt.

EMETINE. $C^{30}H^{44}N^2O^8$ (J. Lefort, *J. Pharm.* [4] ix. 241).—This alkaloïd, discovered by Pelletier and Magendie in 1807 (ii. 485), is best prepared as follows: Powdered ipecacuanha is exhausted, first with alcohol of 86 p. c., then with alcohol of 56 p. c.; the united extracts are evaporated to a syrup over the water-bath, and the residue is treated in a flask with very strong potash-solution (2 pts. potassium hydrate dissolved in a small quantity of water to 100 pts. of the powder), and with a quantity of chloroform equal in bulk to the mixture. The flask must be completely filled with the mixture and closely corked; the whole well agitated and left to stand for several days, till the chloroform has separated; the chloroform then removed with a pipette; and the residue treated with a fresh quantity of chloroform. On distilling off the chloroform, there remains a brown mixture of emetine with a resin, from which the emetine may be extracted by a weak acid, and reprecipitated by ammonia not in excess. A bulky greyish powder is thus obtained, which must be washed, first with water and then with ether, to remove the last traces of resin.

Pure emetine is a very light, whitish, amorphous powder, becoming slightly brown on exposure to the air; it is inodorous, but has a bitter taste; melts at 70° to a dark brown liquid. Water at 15° dissolves only $\frac{1}{1000}$ of its weight of emetine, but acquires thereby an alkaline reaction; alcohol and chloroform dissolve it in all proportions; ether and fixed oils very sparingly. It dissolves very easily in caustic fixed alkalis, less easily in ammonia. With hydrochloric, sulphuric, phosphoric, and acetic acids it forms uncrystallisable salts very soluble in water. It is precipitated by tannic acid, and by a solution of iodine in potassium iodide. With mercuric chloride and potassio-mercuric iodide, it forms compounds sparingly soluble in water; with platinic chloride, a light yellow salt, easily soluble in water, sparingly in alcohol. It is also precipitated from its saline solutions by phosphomolybdic acid and by basic lead acetate.

EPACRIS. The alcoholic extract of the leaves of a species of Epacris from Australia, examined by Rochleder a. Tonner (*Jahresb.* 1861, p. 773; 1866, p. 694), has been found to contain ursone (v. 969), together with fat, wax, and chlorophyll. The leaves also contain a tannin which agrees in all its properties with that of the horse-chestnut, and when treated with hydrochloric acid, yields a red compound exhibiting the composition $C^{26}H^{22}O^{11}.2C^{18}H^{12}O^6$. The same tannin appears also to occur in *Ledum palustre.*

EPICHLORHYDRIN. See CHLORHYDRINS (p. 433).

EPICYANHYDRIN. $C^4H^5NO = (C^3H^5)'''\left\{\begin{matrix}O\\CN\end{matrix}\right.$.—Produced by gently warming epichlorhydrin with aqueous potassium cyanide. A violent action takes place, which may be moderated by cooling, and ultimately epicyanhydrin is deposited in slender laminæ, which are easily purified by washing with water and alcohol, and recrystallisation. The crystals are colourless, soluble in water and alcohol, slightly soluble in ether, and give off large quantities of ammonia when boiled with potash (Pazschke, *Zeitschr. f. Chem.* [2] v. 612).

ERBIUM. See TERBIUM (v. 720).

ERGOTINE. This substance, the active principle of ergot of rye, may be prepared by precipitating the aqueous extract of the ergot with neutral lead acetate, treating the filtrate (free from lead) with mercuric chloride, and precipitating the filtered liquid with phosphomolybdic acid. The ergotine separated from the resulting precipitate by digestion with barium carbonate and water, is a varnish-like brown powder, insoluble in ether and chloroform, and forming amorphous deliquescent salts with acids. Its analysis leads to the formula $C^{50}H^{52}N^2O^3$ (Manassewitz, *Zeitschr. f. Chem.* [2] iv. 154).

ERICINONE. Zwenger a. Himmelmann (*Ann. Ch. Pharm.* cxxix. 203) have shown that this substance is identical with hydroquinone, as originally suggested by Hesse (ii. 500).

ERUCIC ACID. $C^{22}H^{42}O^2$ (ii. 501).—This acid, homologous with acrylic acid, was discovered by Darby (*Ann. Ch. Pharm.* lxix. 1), and has been further examined by Otto (*ibid.* cxxvii. 182; cxxxv. 226) and by Haussknecht (*ibid.* cxliii. 40). It unites directly with *bromine*, when that substance is added to it under water, forming erucic acid dibromide, $C^{22}H^{42}Br^2O^2$, which crystallises by cooling from solution in absolute alcohol, in small white nodular groups of crystals melting between 42° and 43°. Its *barium salt*, $(C^{22}H^{41}Br^2O^2)^2Ba$, and its *lead salt*, $(C^{22}H^{41}Br^2O^2)^2Pb$, are white, viscid, easily decomposible precipitates. *Sodium-amalgam* in alcoholic solution reconverts erucic acid dibromide into erucic acid (Otto).

Erucic acid dibromide heated in sealed tubes to about 145° for seven or eight hours with 4 or 5 mol. *potassium hydrate* in alcoholic solution, yields the potassium salt of benolic acid, $C^{22}H^{40}O^2$ ($= C^{22}H^{42}Br^2O^2 - 2HBr$) (p. 257). But when an alcoholic solution of the dibromide is mixed with alcoholic potash-solution at ordinary temperatures, only 1 mol. hydrobromic acid is abstracted, and monobromerucic acid, $C^{22}H^{41}BrO^2$, is formed, with rise of temperature and separation of potassium chloride. On diluting the solution with water and adding hydrochloric acid, monobromerucic acid is separated in the form of an oil, which soon solidifies. It melts at 33°–34°, and remains liquid for a long time. It is heavier than water and insoluble therein, but dissolves easily in alcohol and ether. It unites with 1 mol. bromine, forming the acid dibromide, $C^{22}H^{41}Br^3O^2$ or $C^{22}H^{41}BrO^2.Br^2$, which melts at 31° to 32°, and forms amorphous viscid salts. This dibromide treated with alcoholic potash gives up hydrobromic acid, but it has not been decidedly made out whether dibromerucic acid is then reproduced by elimination of 1 mol. HBr, or monobromobenolic acid, $C^{22}H^{39}BrO^2$, by elimination of 2HBr.

When erucic acid dibromide is triturated with water and a large excess of *silver oxide*, and the mass, which soon becomes warm and granular, is heated for several hours, till it turns brown, hydrobromic acid is eliminated, and on boiling the mass with water, a yellow oil separates, which is a mixture of liquid oxyerucic acid, $C^{22}H^{42}O^3$, and dioxybenic acid, $C^{22}H^{44}O^4$, the latter of which crystallises out partially after long standing. For complete separation, the oil, after being well washed, is saponified with baryta-water; the precipitate is exhausted with ether; the dissolved barium oxyerucate is decomposed by hydrochloric acid; and the oxyerucic acid, which separates as a yellowish oil, is purified by solution in alcohol. It is viscid, lighter than water, insoluble therein, but miscible in all proportions with alcohol and ether. Its salts, $C^{22}H^{41}O^3M'$, are amorphous, and are all insoluble in water, excepting those of the alkali-metals and of barium. The formation of oxyerucic acid is represented by the equations:

$$\underset{\text{Erucic acid dibromide.}}{C^{22}H^{42}Br^2O^2} + AgOH = \underset{\text{Bromerucic acid.}}{C^{22}H^{41}BrO^2} + H^2O + AgBr.$$

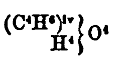
$$\underset{\text{Bromerucic acid.}}{C^{22}H^{41}BrO^2} + AgOH = \underset{\text{Oxyerucic acid.}}{C^{22}H^{42}O^3} + AgBr.$$

This acid may therefore also be formed, though less easily, by treating monobromerucic acid with silver oxide. When boiled with potash-ley, it is converted into dioxybenic acid, $C^{22}H^{44}O^4$, according to the equation, $C^{22}H^{42}O^3 + KOH = C^{22}H^{43}O^4K$ (Haussknecht).

ERYTHREMIC ACID. An acid contained in the blood-red juice of the dragon's blood tree of Brazil (*Croton erythræma*, p. 547).

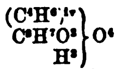
ERYTHRIN or **ERYTHRIC ACID.** $C^{20}H^{22}O^{10}$ (ii. 502).—The following method of preparing this substance from *Rochella fuciformis* is given by Stenhouse (*Chem. Soc. J.* [2] v. 222): Three pounds of the lichen are macerated for twenty minutes in a milk of lime made by slaking ½ lb. of lime in 3 gallons of water, and the partially exhausted weed is then treated with a fresh quantity of milk of lime; a third maceration is found to exhaust the lichen completely. These weak lime-liquors are employed instead of milk of lime for exhausting fresh quantities of the lichen, whilst the first and strongest liquor is filtered rapidly through bag-filters about 6 inches wide and 6 feet long; and the clear liquor, as it passes through, is immediately precipitated by hydrochloric acid, as prolonged contact with the lime decomposes a portion of the erythrin. The precipitated erythrin is collected in bag-filters, and when the greater part of the mother-liquor has been thus removed, it is freed from adhering hydrochloric acid and calcium chloride by stirring it up once or twice with a considerable quantity of water.

The recent experiments of De Luynes (*Ann. Ch. Phys.* [4] ii. 385), Menschutkin (*Bull. Soc. Chim.* [2] ii. 424), and Hesse (*Ann. Ch. Pharm.* cxxxix. 22) have confirmed the view originally put forward by Berthelot, that erythrin is the diorsellinic ether, and picroerythrin the mono-orsellinic ether of erythrite:



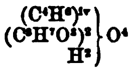
$$\left.\begin{matrix}(C^4H^6)^{iv}\\H^4\end{matrix}\right\}O^4$$

Erythrite.



$$\left.\begin{matrix}(C^4H^6)^{iv}\\C^8H^7O^3\\H^3\end{matrix}\right\}O^4$$

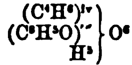
Picroerythrin.



$$\left.\begin{matrix}(C^4H^6)^{iv}\\(C^8H^7O^3)^2\\H^2\end{matrix}\right\}O^4$$

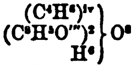
Erythrin.

Grimaux (*Bull. Soc. Chim.* [2] iii. 410), regarding orsellinic acid, $C^8H^8O^4$, as a triatomic and monobasic acid, $\left.\begin{matrix}(C^8H^5O)'''\\H^3\end{matrix}\right\}O^3$, represents erythrin and picroerythrin by the following formulæ:



$$\left.\begin{matrix}(C^4H^6)^{iv}\\(C^8H^5O)'''\\H^5\end{matrix}\right\}O^6$$

Picroerythrin.



$$\left.\begin{matrix}(C^4H^6)^{iv}\\(C^8H^5O''')^2\\H^6\end{matrix}\right\}O^8$$

Erythrin.

According to Hesse (*Jahresb.* 1866, p. 658), erythrin in the air-dried state retains 6 p. c. water = $2C^{20}H^{22}O^{10}.3H^2O$, which is given off partly over sulphuric acid, completely at 100°. The *lead salt* contains $(C^{20}H^{19}O^{10})^2Pb^3.3H^2O$; *bromerythrin* is $2C^{20}H^{19}Br^3O^{10}.3H^2O$.

Erythrin boiled with absolute *alcohol* yields picroerythrin and ethyl orsellinate (ii. 502); with hydrated alcohol the same products are obtained, but the proportion of ethyl orsellinate is smaller, because part of the erythrin is decomposed by the water of the alcohol, in such a manner as to yield orcin and carbon dioxide:

$$\underset{\text{Erythrin.}}{C^{20}H^{22}O^{10}} + \underset{\text{Alcohol.}}{C^2H^6O} = \underset{\text{Picro-erythrin.}}{C^{12}H^{16}O^7} + \underset{\text{Ethyl Orsellinate.}}{C^8H^7(C^2H^5)O^4}$$

$$\underset{\text{Erythrin.}}{C^{20}H^{22}O^{10}} + H^2O = \underset{\text{Picro-erythrin.}}{C^{12}H^{16}O^7} + \underset{\text{Orcin.}}{C^7H^8O^2} + CO^2.$$

With *ether*, erythrin behaves indifferently, dissolving in 328 pts. at 20°. Boiled with *amyl alcohol*, it yields amyl orsellinate and picroerythrin, both of which crystallise. This reaction affords an easy method of obtaining perfectly pure picroerythrin. When the decomposition is complete, the remaining amyl alcohol is distilled off, whereupon the amyl orsellinate gradually separates as a colourless oil, while the picroerythrin separates from the liquid filtered at about 40° in white silky efflorescent needles containing $C^{12}H^{16}O^7.3H^2O$ (Hesse, *loc. cit.*).

BETA-ERYTHRIN. $C^{21}H^{24}O^{10}$.—This body, homologous with erythrin, was discovered by Menschutkin (*Bull. Soc. Chim.* [2] ii. 424; *Jahresb.* 1864, p. 548), not by Lamparter, as stated in vol. iv. p. 641. It is prepared from certain varieties of *Rochella fuciformis* (the South American varieties, according to Lamparter) by digestion with lukewarm dilute lime-water (Menschutkin), cold milk of lime (Lamparter), precipitation with sulphuric or hydrochloric acid, and crystallisation from alcohol. It separates as a white crystalline powder containing $C^{21}H^{24}O^{10}.H^2O$, soluble in alcohol and ether, nearly insoluble in water, and decomposed by alcohol or water at the boiling heat, yielding β picroerythrin, $C^{13}H^{16}O^6$, and orsellinic acid or orsellinic ether (ii. 611). β erythrin is coloured transiently red by *chloride of lime*; its solution in ammonia forms with *silver nitrate* a reddish, easily reducible precipitate; with *basic lead acetate*, a gelatinous precipitate having nearly the composition $C^{21}H^{20}Pb^2O^{10}$ (Menschutkin).

β picroerythrin boiled with saturated *baryta-water* is resolved into carbon dioxide, erythrite, and β orcin (Menschutkin):

$$\underset{\beta\text{ Picro-erythrin.}}{C^{13}H^{16}O^6} + 2H^2O = \underset{\text{Erythrite.}}{C^4H^{10}O^4} + \underset{\beta\text{ Orcin.}}{C^8H^{10}O^2} + CO^2.$$

ERYTHRITE. $C^4H^{10}O^4 = \left.\begin{matrix}(C^4H^6)^{iv}\\H^4\end{matrix}\right\}O^4$. *Erythromannite*, *Erythroglucin*, *Phycite* (ii. 504).—To prepare this substance from erythrin, Stenhouse (*loc. cit.*) dissolves the latter in a slight excess of milk of lime, and boils it for half an hour in a vessel furnished with a long condensing tube, so as to exclude the air, and thereby prevent, in a great measure, as observed by De Luynes (*Jahresb.* 1863, p. 502), the formation of a deep red-coloured resinous substance. The solution, now containing orcin and erythrite, is filtered, the excess of lime removed by a stream of carbonic acid—or more conveniently, on the large scale, by exact neutralisation with dilute sulphuric acid—and evaporated to dryness, first over a sand-bath, finally over a water-bath. The orcin is dissolved out of the residue by repeated digestion with benzol (boiling between 110° and 150°) in a metallic vessel connected with a condenser and heated in a paraffin-bath; and the undissolved portion treated with boiling water gives up the erythrite, which may be purified by washing with cold alcohol and recrystallisation from water.

Erythrite exhibits in a high degree the phenomenon of surfusion. When heated nearly to its boiling point, it forms a mobile liquid, viscid after cooling, which sometimes crystallises spontaneously at ordinary temperatures, but mostly not till it is agitated, the solidification being then attended with considerable rise of temperature. Its concentrated aqueous solution in contact with *platinum-black* absorbs oxygen so rapidly that the mass becomes red hot; with a dilute solution the oxidation is more gradual and an acid is formed (*infra*). *Lime* dissolves in an aqueous solution of erythrite more abundantly than in pure water; the solution coagulates when heated, and alcohol throws down from it a compound of erythrite and lime. Erythrite heated to 240° with *potassium hydrate* forms oxalic and acetic acids, with evolution of hydrogen. With fuming *hydriodic acid* it yields secondary butyl iodide, or butylene hydriodide, C^4H^8HI (ii. 505; v. 736). With *phosphorus pentachloride* or *chlorine* in sunshine, it yields hydrochloric acid and a viscid uncrystallisable substance.

The *chlorhydrin of erythrite*, $(C^4H^6)^{iv}\left\{\begin{matrix}Cl^2\\(OH)^2\end{matrix}\right.$, is produced by heating erythrite to 100° for about a hundred hours with 12 to 15 pts. concentrated hydrochloric acid in very strong tubes, and evaporating the product over potash-lime. The crystals are purified by recrystallisation from ether, with addition of a little animal charcoal; they dissolve easily in water, alcohol, and ether; melt at 145°; and volatilise in white vapours which condense to crystals (De Luynes, *Ann. Ch. Phys.* [4] ii. 385; *Jahresb.* 1864, p. 497).

ERYTHRITIC or **ERYTHROGLUCIC ACID.** $C^4H^8O^5 = \left.\begin{matrix}(C^4H^4O)^{iv}\\H^4\end{matrix}\right\}O^4$.— This acid, related to erythrite in the same manner as glyceric acid to glycerin, is produced by the oxidation of erythrite in contact with platinum-black, or by the action of nitric acid. It was first observed by De Luynes (*supra*), and has been further examined by Sell (*Bull. Soc. Chim.* [2] v. 384), and by Lamparter (*Ann. Ch. Pharm.* cxxxiv. 243), whose descriptions of its lead salts do not however quite agree.

Sell prepares the acid by leaving a solution of 30 grms. erythrite in 250 to 300 grms. water in contact with 15 to 20 grms. platinum-black previously mixed with pumice, renewing the water from time to time as it evaporates. The liquid then acquires a strong acid reaction, and if filtered after all the erythrite has disappeared, then evaporated to one-half, and mixed with basic lead acetate, yields a yellowish-white precipitate, which must be purified by decomposing it with hydrogen sulphide, reprecipitating with basic lead acetate, and repeating this treatment several times till the lead precipitate becomes perfectly white. It then yields a colourless solution of the acid, which, however, when evaporated over the water-bath, turns yellow and then brown, giving off the odour of caramel. The syrupy acid when left in a vacuum, partly solidifies to a crystalline mass which deliquesces on exposure to the air. The lead salt obtained as above is, according to Sell, a basic salt containing $C^{16}H^{26}Pb^5O^{22}$ or $4C^4H^6O^5Pb.PbH^2O^2$. The other salts of erythritic acid are easily soluble. Silver nitrate produces in the aqueous solution of the acid a white precipitate which is reduced in a few minutes, with deposition of a silver speculum; lime-water produces a slight turbidity which disappears on the addition of a drop of acetic acid.

Lamparter prepares erythritic acid by oxidising erythrite in warm concentrated solution with fuming nitric acid (with dilute nitric the chief product is oxalic acid). The product is a gummy acid whose *barium salt* is precipitated from its aqueous solution by alcohol, in the form of a powder having the composition $C^4H^6O^5Ba + H^2O$. The *lead salt* obtained by precipitation with basic lead acetate is, according to Lamparter, a normal salt, having when dried at 160° the composition $C^4H^6O^5Pb$.

ERYTHROBENZENE. A red colouring matter prepared from nitrobenzene by leaving 12 pts. of that substance in contact with 24 pts. of fine iron-filings and 6 pts. strong hydrochloric acid, for 24 hours at ordinary temperatures. The solid mass is then pulverised, and exhausted with water, and the clear solution is precipitated with common salt. The colouring matter thus obtained is purified by again dissolving and precipitating it (F. Laurent a. J. Castlehaz, *Repertory of Patent Inventions*, Oct. 1862, p. 339; *Dingl. pol. J.* clvi. 239).

ERYTHROCENTAURIN. $C^{27}H^{24}O^{8}$ (C. Mehu, *J. Pharm.* [4] iii. 265).—A substance allied to santonin, obtained from the common centaury (*Erythræa Centaurium*, Gentianaceæ). To prepare it, the aqueous extract of the flower-heads, or of the entire plant, is treated with 4 or 5 times its weight of alcohol; the syrupy residue of the alcoholic extract is repeatedly agitated with 4 vol. ether; and the ethereal solution is evaporated, whereby a yellowish-brown semifluid residue is obtained, which after a while yields crystals of impure erythrocentaurin. These, after being pressed and once recrystallised from water, are decolorised in ethereal solution by animal charcoal. On leaving the ether to evaporate, large colourless crystals are obtained, amounting to scarcely $\frac{1}{3}$ per thousand of the weight of the dried plant.

Pure erythrocentaurin is tasteless and inodorous, neutral and not hygroscopic, not volatile; melts at 136°, and solidifies again in the crystalline form. Its solution in chloroform neither acts on polarised light nor fluoresces. It dissolves in 1630 pts. water at 15°, in about 13·5 pts. at 100°, in 48 pts. of 86 p. c. alcohol at 15°, in 13·5 pts. chloroform, and 245 pts. ether; easily also in oils both fixed and volatile, in benzol, and in carbon bisulphide. Acids increase its solubility in water, but do not unite with it; from its colourless solution in strong sulphuric acid it is precipitated by water without alteration. It is not acted upon by nitric, hydrochloric, or chromic acid, bromine, iodine, or alkalis; when fused in chlorine gas, it is converted into a glutinous substance recrystallisable only from ether. Erythrocentaurin is decomposed by potassium permanganate, even at ordinary temperatures. When exposed to sunshine, it quickly acquires a bright red colour, but without alteration of weight or of its relations to solvents. This coloured erythrocentaurin yields colourless solutions which in the dark deposit colourless crystals. The red colour likewise disappears on heating the substance to about 130°. The coloration of erythrocentaurin (like that of santonin) is produced only by the most refrangible (blue or violet) rays of the spectrum; but santonin which has been turned yellow by light is not decolorised by heat.

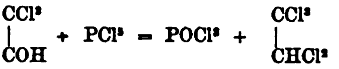
ERYTHROGLUCIC ACID. Syn. with ERYTHRITIC ACID (p. 583).

ETHANE. $C^{2}H^{6} = \begin{matrix} CH^{3} \\ | \\ CH^{3} \end{matrix} = C\left\{\begin{matrix} CH^{3} \\ H^{3} \end{matrix}\right.$. *Ethyl Hydride, Methyl, Dimethyl* (ii. 533; iii. 984).—This gas is evolved, together with carbon dioxide, by heating barium dioxide with acetic anhydride, barium acetate being produced at the same time (Schützenberger, *Bull. Soc. Chim.* [2] v. 278):

$$2(C^{2}H^{3}O)^{2}O + BaO^{2} = (C^{2}H^{3}O^{2})^{2}Ba + 2CO^{2} + C^{2}H^{6}.$$

Darling (*Chem. Soc. J.* [2] vi. 426) finds that this reaction is apt to give rise to violent explosion [arising from the formation of acetyl peroxide, i. 35], which, however, may be prevented by mixing the barium dioxide with dry sand. The gas then evolved consists, after removal of carbon dioxide, chiefly of methane (marsh gas) with a little carbon monoxide and about 17 p. c. ethane. Frankland's mode of preparation by heating methyl iodide with zinc, yields perfectly pure ethane; but is not well adapted for the preparation of large quantities. The best process is the electrolysis of potassium acetate. Darling's experiments fully confirm the results obtained by Schorlemmer (iii. 984) respecting the identity of the gas obtained by this process with that obtained from mercuric ethide. When treated with chlorine in diffused daylight, it is converted into a mixture of ethyl chloride, $C^{2}H^{5}Cl$, and chlorethyl chloride, $C^{2}H^{4}Cl^{2}$. The ethyl chloride thus obtained was converted into acetate, which by saponification with potash yielded pure ethyl alcohol.

Pentachlorethane. $C^{2}HCl^{5}$ (Paterno, *Compt. rend.* lxviii. 450).—Produced by the action of phosphorus pentachloride on anhydrous chloral:



$$\begin{matrix} CCl^{3} \\ | \\ COH \end{matrix} + PCl^{5} = POCl^{3} + \begin{matrix} CCl^{3} \\ | \\ CHCl^{2} \end{matrix}$$

A small quantity of the pentachloride is added to chloral contained in a retort fitted with an upright condenser; the mixture is warmed; another portion of pentachloride added as soon as the first action is over, the process being repeated till 1 mol. PCl^{5} has been added to 1 mol. chloral; and the reaction is completed by heating the mixture for some hours to the boiling point. Water is then added, and the separated pentachlorethane is dried over calcium chloride and rectified. It is a colourless oil, smelling like chloroform, boiling without decomposition at 158°, having a sp. gr. of 1·71 at 0°, 1·69 at 13°, soluble in alcohol and ether. It remains liquid at −18°, but is easily solidified by the cold produced by evaporation of sulphurous anhydride. Heated in sealed tubes to 250° with phosphorus pentachloride, it is converted into hexchlorethane or carbon trichloride, C^2Cl^6:

$$C^2HCl^5 + PCl^5 = C^2Cl^6 + PCl^3 + HCl.$$

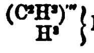
It is also converted into carbon trichloride by exposure to sunshine.

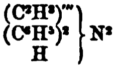
Pentachlorethane obtained as above is most probably identical with Regnault's tetrachlorinated ethyl chloride (ii. 530) and trichlorethylene chloride (ii. 573), the former of which is described as boiling at 148°, the latter at 154°, the differences being probably due to the admixture of Regnault's compounds with other substitution-products formed at the same time. The compound boiling at 180°–181°, and said to contain C^2HCl^5, which Hübner obtained among the products of the action of phosphorus pentachloride or acetyl chloride, was probably carbon trichloride.

The action of the pentachloride on chloral yields also a small quantity of a scaly crystalline compound, not yet analysed, which does not volatilise with vapour of water (Paterno).

ETHENE. Syn. with ETHYLENE.

ETHENYL. C^2H^3.—The triatomic radicle derived from ethane by abstraction of 3 at. hydrogen.

ETHENYL-DIAMINE.  $\left.\begin{matrix}(C^2H^3)'''\\H^3\end{matrix}\right\}N^2$.—This is the composition of acediamine (i. 2).

Ethenyl-diphenyl-diamine. $C^{14}H^{14}N^2 =$  $\left.\begin{matrix}(C^2H^3)'''\\(C^6H^5)^2\\H\end{matrix}\right\}N^2$ (Hofmann, *Compt. rend.* lxii. 729; *Bull. Soc. Chim.* [2] vi. 162).—This base, homologous with methenyl-[formyl-] diphenyl-diamine (iv. 459), is produced by the action of phosphorus trichloride on aniline mixed with phenyl-acetamide, or better with acetyl chloride, or better still with acetic acid:

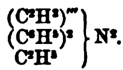
$$\underset{}{3C^6H^7N} + \underset{\substack{\text{Phenyl-}\\\text{acetamide.}}}{3C^8H^9NO} + PCl^3 = 3HCl + H^3PO^3 + 3C^{14}H^{14}N^2.$$

$$6C^6H^7N + \underset{\substack{\text{Acetyl}\\\text{chloride.}}}{3C^2H^3OCl} + PCl^3 = 6HCl + H^3PO^3 + 3C^{14}H^{11}N^2.$$

$$\underset{\text{Aniline.}}{6C^6H^7N} + \underset{\text{Acetic acid.}}{3C^2H^4O^2} + 2PCl^3 = 6HCl + 2H^3PO^3 + \underset{\substack{\text{Ethenyl-diphenyl-}\\\text{diamine.}}}{3C^{14}H^{14}N^2}$$

A cooled mixture of 3 pts. aniline and 2 pts. acetic acid is gradually mixed with 2 pts. phosphorus trichloride, and the viscid liquid is heated for some hours to 160°. The resulting light-brown friable resinous mass is dissolved in boiling water, and the cooled filtrate is mixed with caustic soda, which throws down the base as a white crystalline precipitate, to be purified by recrystallisation from alcohol. It forms white laminæ melting at 137°, volatilising without decomposition at a very high temperature, nearly insoluble in water, sparingly soluble in cold, easily in hot alcohol, in ether and in acids. Its *platinochloride*, $2(C^{14}H^{14}N^2.HCl).PtCl^4$, is sparingly soluble and crystalline; the *nitrate*, $C^{14}H^{14}N^2.HNO^3$, separates at first as an oil, which afterwards becomes crystalline. The base is attacked by strong sulphuric acid, which eliminates acetic acid and forms phenylsulphamic or sulphanilic acid:

$$C^{14}H^{11}N^2 + 2SO^4H^2 = C^2H^4O^2 + 2C^6H^7NSO^3.$$

Ethenyl-ethyl-diphenyl-diamine. $C^{16}H^{18}N^2 +$  $\left.\begin{matrix}(C^2H^3)'''\\(C^6H^5)^2\\C^2H^5\end{matrix}\right\}N^2$. — Ethenyl-diphenyl-diamine heated with ethyl iodide for several hours, forms a crystalline iodide, which may be converted into a chloride by treatment with chloride of silver; and this chloride treated with soda-ley yields ethenyl-ethyl-diphenyl-diamine, as a viscid oil insoluble in water and destitute of alkaline reaction. This oil is attacked by *methyl-iodide* at 100°, and the iodide thus produced is converted by silver oxide into a strongly alkaline liquid containing the ammonium-base, $\left.\begin{matrix}(C^2H^3)'''\\(C^6H^5)^2\\C^2H^5\\CH^3\\OH\end{matrix}\right\}\begin{matrix}N^v\\|\\N^v\end{matrix}$

Methyl-aniline treated with phosphorus trichloride and acetic acid yields a chloride, which is converted by silver oxide into an alkaline ammonium-base homologous with the preceding and represented by the formula, $\left.\begin{matrix}(C^2H^3)'''\\(C^6H^5)^2\\(CH^3)^2\\OH\end{matrix}\right\}N^2$.

Ethenyl-dinaphthyl-diamine, $C^{22}H^{18}N^2 = \left.\begin{matrix}(C^2H^3)'''\\(C^{10}H^7)^2\\H\end{matrix}\right\}N^2$, is produced from naphthylamine in the same manner as ethenyl-diphenyl-diamine from aniline. This base is a tough resinous mass, yielding a platinochloride whose analysis leads to the formula just given.

Ethenyl-ditolyl-diamine, $C^{16}H^{18}N^2 = \left.\begin{matrix}C^2H^3\\(C^7H^7)^2\\H\end{matrix}\right\}N^2$, obtained by the action of PCl^3 on toluidine and acetic acid, is scarcely distinguishable from the diphenylated base.

Ethenyl-triphenyl-diamine, $C^{20}H^{18}N^2 = \left.\begin{matrix}(C^2H^3)'''\\(C^6H^5)^3\end{matrix}\right\}N^2$, is produced by the action of phosphorus trichloride on a mixture of 1 mol. diphenylamine and 1 mol. phenylacetamide:

$$\left.\begin{matrix}(C^6H^5)^2\\H\end{matrix}\right\}N + \left.\begin{matrix}C^2H^3O\\C^6H^5\\H\end{matrix}\right\}N = H^2O + \left.\begin{matrix}(C^2H^3)'''\\(C^6H^5)^3\end{matrix}\right\}N^2.$$

ETHERS. *Formation of Compound Ethers by the mutual action of Acids and Alcohols.*—The first part of the researches of Berthelot a. Péan de St. Gilles on this subject was noticed in vol. ii. p. 210 of this Dictionary. In a continuation of this research (*Bull. Soc. Chim.* v. 182, and [2] i. 336; in detail, *Ann. Ch. Phys.* [3] lxviii. 225), the authors direct attention especially to the limit of combination between different acids and alcohols; the variations of this limit resulting from excess of acid, alcohol, neutral ether, or water; the action of acids on very dilute alcohols; and the result of the simultaneous action of several acids on several alcohols.

1. In a homogeneous mixture of acid, alcohol, compound ether, and water, the *limit of combination* is reached when the ether-forming affinity of the acid for the alcohol, and the ether-decomposing power of the water, are equal to one another. The existence of such a limit is proved by causing alcohol and acid on the one hand, and the corresponding compound ether with an equivalent quantity of water on the other (this mixture being exactly similar to the former in ultimate composition), to act upon one another for different times and at different temperatures. It is then found that if, in the first case, two-thirds of the whole quantity of acid has entered into combination, then in the second, one third of the neutral ether will be resolved into acid and alcohol.

That this limit of combination is almost independent of the particular nature of the acid and alcohol, and depends essentially on the equivalent proportions of the mixture, had been shown by the authors in the first part of their research, as far as regards particular systems (ii. 510); and this result is now shown to be universally true, not only with respect to the action of mono-acid or poly-acid alcohols on monobasic or polybasic acids, when these bodies act upon one another without the presence of water, but likewise for the most various mixtures, whether they contain excess of acid, or of alcohol, or of compound ether, or of water. The particular nature of the alcohol and of the acid does however exert a slight influence, at least in the case of monatomic compounds, inasmuch as metameric mixtures (*e.g.* amyl alcohol and acetic acid, ethyl alcohol and valeric acid) always exhibit slightly different limits; with polyatomic alcohols and acids, however, no such differences are observed.

A remarkable difference is observed between the behaviour of polybasic acids and that of polyacid alcohols, inasmuch as a molecule of a bibasic acid etherifies the same quantity of alcohol as 2 molecules of a monobasic acid, and a molecule of a tribasic acid etherifies the same quantity of alcohol as 3 molecules of a monobasic acid, whereas a molecule of a biacid or triacid alcohol—at least, if no great excess of acid is present—unites with only the same quantity of acid as a molecule of a monoacid alcohol. The cause of this difference of behaviour—which seems to show that the functions of the acid and of the alcohol in etherification are not exactly alike—is to be found in the fact that a polybasic acid forms only *one* neutral compound with a monoacid base, whereas the several compounds which may be formed from a polyacid alcohol and a monobasic acid (mono-, di-, and tri-acetin for example) are all destitute of acid properties.

2. When an excess of alcohol acts upon a molecule of acid, the quantity of compound ether formed increases regularly (not by sudden increments) with the augmentation in the quantity of alcohol, and tends towards the complete fixation of the acid; the quantity of acid which in presence of an excess of alcohol does not enter into combination, is nearly in inverse proportion to the total quantity of the latter, and directly proportional to the total quantity of the acid. In this case, also, monoacid and polyacid alcohols react nearly in the same manner with one and the same monobasic acid. The following table shows the quantities per cent. of various acids which entered into combination when 1 mol. of the acid was acted upon by *n* molecules of an alcohol:

Methyl alcohol	Acid	Ethyl alcohol	Acid	Amyl alcohol	Acid	Glycerin	Acid
n = 1	67·5	*n* = 1	66·5	*n* = 1	68·2	*n* = 1	68·7
1·5	75·9	1·5	77·9	—	—	1·5	72·0
2	84·0	2	82·8	2	86·9	—	—
—	—	3	88·2	3	89·4	—	—
—	—	—	—	—	—	6·1	89·3
19	95·0	—	—	—	—	—	—
500	100·0*	—	—	—	—	—	—

In like manner, the quantity of an alcohol etherified under the influence of an excess of one monobasic or polybasic acid, increases with the amount of this excess, and appears, when more than two molecules of acid act upon one molecule of alcohol, to be directly proportional to the total quantity of the acid. Traces of alcohol are taken up by excess of acid with nearly the same degree of completeness as traces of acid by an alcohol. Polyacid alcohols appear, moreover, in presence of excess of acid, to take up a larger quantity of the acid in proportion to their atomicity.

3. Etherification is retarded by addition either of a neutral ether or of water. But just as compound ethers are not completely decomposed, even by large quantities of water, so likewise is their formation not entirely prevented by the presence of large quantities of water; the amount of ether produced sinks to a minimum when the acid and alcohol are present in equivalent quantities, and is increased by the presence of an excess either of acid or of alcohol. In mixtures containing 8 mol. water (H^2O) to 1 mol. alcohol, and containing excess of alcohol, the quantity of ether formed is nearly proportional to the quantity of acid present; an almost exact proportionality is observed in mixtures diluted to the extent which is found in fermented liquors (23 to 48 mol. water to 1 mol. alcohol).

The phenomena exhibited in the action of water on compound neutral ethers are the converse of those which take place in their formation. A trace of water decomposes a nearly equivalent quantity of an ether into acid and alcohol; the decomposition of the ether increases with the quantity of water in the mixture, and becomes nearly perfect when only traces of ether are present.

4. In the simultaneous action of several alcohols on an acid, or of several acids on an alcohol, or finally of several monoacid or polyacid alcohols on several monobasic or polybasic acids, the sum of the compound ethers formed is equivalent to that produced by the corresponding quantity of a single alcohol on a single acid.

Formation of Ethers by Oxidation of Fatty Acids.—Strecker observed some years ago that butyric acid oxidised with manganese dioxide and sulphuric acid yields an ethereal product. This reaction has lately been further investigated by Veiel (*Ann. Ch. Pharm.* cxlviii. 160), who finds that when pure butyric acid is gradually dropped upon a mixture of pulverised manganese dioxide and sulphuric acid diluted with an equal volume of water, and the mixture is distilled, an ethereal liquid is obtained which, after purification in the usual way, boils between 116° and 145°, has a composition expressed approximately by the formula $C^4H^{12}O^2$, and when decomposed by potash yields only butyric acid and alcohols: hence Veiel infers that it consists mainly of propyl butyrate, $C^7H^{14}O^2$, mixed with lower homologues. Valeric acid treated in a similar manner yielded an ether having the composition of methyl valerate, $C^6H^{12}O^2$, and yielding valeric acid by saponification. No non-volatile products were obtained.

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* The mixture did not redden litmus.

Action of Bromine on Ethers (Ladenberg a. Wichelhaus, *Ann. Ch. Pharm.* clii. 163).—Oxygen-ethers in which the alcohol-radicle is immediately associated with a carboxyl group, such as ethyl acetate, $CH^3—COOC^2H^5$, ethyl oxalate, $COOH—COOC^2H^5$, &c., are not attacked by bromine; but those in which the alcohol-radicle does not enter in this manner, such as ethyl-orthocarbonate, $C(OC^2H^5)^4$, yield ethyl bromide when thus treated. *Orthoformic ether*, $CH(OC^2H^5)^3$, produced by the action of chloroform on sodium ethylate (p. 621), is attacked by bromine in the cold, and the product when distilled yields ethyl bromide, ethyl metacarbonate (ordinary carbonic ether), ordinary ethyl formate, and alcohol; thus:

$$\underset{\text{Orthoformate.}}{2CH(OC^2H^5)^3} + Br^2 = \underset{\text{Bromide.}}{2C^2H^5Br} + \underset{\text{Carbonate.}}{CO(OC^2H^5)^2} + \underset{\text{Formate.}}{CHO(OC^2H^5)} + \underset{\text{Alcohol.}}{C^2H^6O}$$

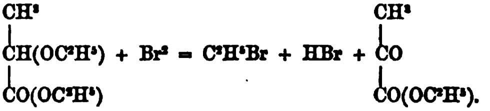
Ethyl orthocarbonate heated with bromine yields ethyl bromide, ethyl metacarbonate, and a small quantity of bromal, resulting from the further action of the bromine on the ethyl oxide likewise produced in the first instance:

$$\underset{\text{Orthocarbonate.}}{C(OC^2H^5)^4} + Br^x = \underset{\text{Metacarbonate.}}{CO(OC^2H^5)^2} + [(C^2H^5)^2O + Br^x].$$

Ethyl metacarbonate heated with bromine also yields ethyl bromide and bromal, with evolution of carbon dioxide:

$$CO(OC^2H^5)^2 + Br^x = CO^2 + [(C^2H^5)^2O + Br^x].$$

Ethyl-glycollic acid, $\begin{array}{l} CH^2(OC^2H^5) \\ | \\ COOH \end{array}$, heated with bromine yields ethyl bromide, and probably also glyoxylic and glycollic acids. *Ethyl-lactic ether* is attacked by bromine at 100°, yielding ethyl bromide, hydrogen bromide, and a liquid which distils between 120° and 250°, probably pyroracemic ether:



$$\begin{array}{l} CH^3 \\ | \\ CH(OC^2H^5) \\ | \\ CO(OC^2H^5) \end{array} + Br^2 = C^2H^5Br + HBr + \begin{array}{l} CH^3 \\ | \\ CO \\ | \\ CO(OC^2H^5). \end{array}$$

Action of Alcohols upon Ethers.—Oxygen-acid ethers and haloïd ethers are decomposed by heating with alcohols, the two alcohol-radicles changing places. Thus when ethyl silicate is heated to 160°–180° with amyl alcohol, amyl silicate is formed, together with ethyl alcohol. A mixture of amyl iodide with rather more than 2 mol. ethyl alcohol heated for 24 hours to 160°–180°, yields water, ethyl-amyl oxide, and ethyl iodide:

$$C^5H^{11}I + 2(C^2H^5HO) = H^2O + C^2H^5I + \left.\begin{array}{r} C^2H^5 \\ C^5H^{11} \end{array}\right\} O.$$

A similar reaction takes place between ethyl iodide and amyl alcohol. In like manner ethyl acetate and amyl alcohol yield water, amyl acetate, and ethyl-amyl oxide. Ethyl benzoate, and especially ethyl chloride, are but slowly decomposed. Ethyl oxalate heated to 220°–250° for 36 hours with 1 mol. amyl alcohol is partially decomposed, yielding carbon dioxide, carbon monoxide, ethyl oxide, ethyl alcohol, amyl oxalate, and probably also ethyl-amyl oxide. Those ethers which are easily decomposible by water are also decomposed with more or less facility by alcohols, but apparently only by an action of masses, and not on account of the greater affinity of the alcohol to the acid (Friedel a. Crafts, *Ann. Ch. Pharm.* cxxx. 198).

A mixture of ethyl iodide and amyl alcohol, or of amyl iodide and ethyl alcohol, in equivalent quantities, yields hydriodic acid and ethyl-amyl oxide, according to the equation:

$$\left.\begin{array}{r} C^5H^{11} \\ H \end{array}\right\} O + C^2H^5I = HI + \left.\begin{array}{r} C^2H^5 \\ C^5H^{11} \end{array}\right\} O.$$

The hydriodic acid thus formed acts upon the amylic or ethylic alcohol in such a manner as to form ethylic or amylic iodide and water, and, on the other hand, this water may act upon the ethylic or amylic iodide so as to reproduce the alcohols, the reaction taking place one way or the other till an equilibrium is established. In this manner a small quantity of an alcoholic iodide may, by successive and alternating transformations, etherify a considerable quantity of alcohol, without any essential diminution of the quantity of the iodide (Friedel a. Crafts, *Ann. Ch. Pharm.* cxxxi. 55).

According to H. Gal (*Compt. rend.* lix. 1049), the methylic and ethylic ethers of the formic, benzoic, or oxalic series saturated with dry *hydrogen bromide* and heated to 100°, are completely resolved into free acid and the bromide of the alcohol-radicle. Ethyl carbonate is resolved under these circumstances into ethyl bromide, carbon dioxide, and water; ethyl nitrate yields ethyl bromide and a considerable quantity of red vapours.

Action of Alkali-metals.—The action of alkali-metals on oxygen-ethers has given rise to considerable discussion. Löwig a. Weidmann (*Pogg. Ann.* l. 98), by heating ethyl acetate with potassium, obtained potassium ethylate and a liquid which reduced silver salts: they did not observe any evolution of hydrogen. L. Gmelin (*Handbook*, viii. 499) explained their results by the following equation:

$$\underset{\text{Ethyl acetate.}}{C^2H^3(C^2H^5)O^2} + K^2 = \underset{\substack{\text{Potassium}\\ \text{ethylate.}}}{C^2H^5KO} + \underset{\substack{\text{Potassium}\\ \text{aldehyde.}}}{C^2H^3KO}$$

Geuther (*Arch. Pharm.* [2] cxvi. 97; *Jahresb.* 1863, p. 323) found that when ethyl acetate purified from alcohol by repeated rectification over sodium was heated with sodium, the metal dissolved, with evolution of hydrogen and formation of sodium ethylate, and the sodium salt of an acid, $C^6H^{10}O^3$, which he regards as *ethyl-diacetic acid*, $C^4H^5(C^2H^5)O^3$:

$$\underset{\text{Ethyl acetate.}}{2C^2H^3(C^2H^5)O^2} + Na^2 = \underset{\substack{\text{Sodium}\\ \text{ethylate.}}}{C^2H^5NaO} + \underset{\substack{\text{Sodium}\\ \text{ethyl-}\\ \text{diacetate.}}}{C^6H^9NaO^3} + H^2.$$

Frankland a. Duppa (*Chem. Soc. J.* [2] iv. 396; v. 102; *Jahresb.* 1865, p. 304) have also examined the action of sodium on ethyl acetate and other compound ethers of the fatty series, with results partly agreeing with those of Geuther. They find that when acetic ether is heated with sodium to 130° in a flask provided with an inverted condensing apparatus, two reactions go on simultaneously, both being attended with evolution of hydrogen. (1) The sodium acts in such a manner as to produce alcohol, together with the monosodic and disodic salts of Geuther's ethyl-diacetic acid (to which salts, however, they assign different names and rational formulæ, p. 591); thus:

$$4C^2H^3(C^2H^5)O^2 + Na^2 = 2C^6H^9NaO^3 + 2C^2H^6O + H^2$$

and

$$2C^2H^3(C^2H^5)O^2 + Na^2 = C^6H^8Na^2O^3 + C^2H^6O + H^2.$$

(2) The sodium simply displaces an equivalent quantity of hydrogen in one or in two molecules of acetic ether, producing the ethylic ethers of sodacetic and disodacetic acids:

$$2(C^2H^3O^2.C^2H^5) + Na^2 = 2(C^2H^2NaO^2.C^2H^5) + H^2$$

and

$$C^2H^3O^2.C^2H^5 + Na^2 = C^2HNa^2O^2.C^2H^5 + H^2.$$

These several sodium-compounds when heated with ethyl-iodide are converted into ethers in which the sodium is replaced by an equivalent quantity of ethyl. The sodium compounds, in fact, were not separated and analysed, but their composition was inferred from that of the several ethylic compounds, $C^2H^2(C^2H^5)O^2.C^2H^5$, &c., obtained by treating the crude product of the action of sodium with ethylic iodide, and fractionating the resulting distillate.

The action of sodium on ethyl acetate and other compound ethers has also been studied by Wanklyn (*Chem. News*, 1868, pp. 121, 143; *Zeitschr. f. Chem.* [2] iv. 673; further, *Chem. News*, 1870, p. 7), who obtains the same products as Geuther, with exception of the free hydrogen. Wanklyn finds indeed, in accordance with Löwig a. Weidmann, that when sodium acts upon perfectly pure ethyl-acetate, no hydrogen *is* evolved as a direct result of the reaction, the only products being sodium ethylate and sodium triacetyl, $(C^2H^3O)^3Na$, identical with Geuther's sodium-ethyl-diacetate:

$$3\left[\left.\begin{matrix}C^2H^3O\\ C^2H^5\end{matrix}\right\}O\right] + Na^4 = 3\left[\left.\begin{matrix}C^2H^5\\ Na\end{matrix}\right\}O\right] + \left.\begin{matrix}(C^2H^3O)^3\\ Na\end{matrix}\right\}.$$

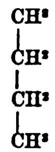
A secondary reaction, however, takes place at the same time between the sodium ethylate and the excess of ethyl acetate, resulting in the formation of ethylene-sodium acetate and alcohol:

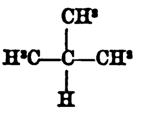
$$\left.\begin{matrix}C^2H^3O\\C^2H^5\end{matrix}\right\}O + \left.\begin{matrix}C^2H^5\\Na\end{matrix}\right\}O = \left.\begin{matrix}C^2H^4Na\\C^2H^3O\end{matrix}\right\}O + \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O;$$

and the sodium acting on the alcohol thus produced converts it into sodium ethylate, with elimination of hydrogen; but the quantity of hydrogen thus evolved is always much less than the equivalent of the quantity of sodium dissolved. When only a slight excess of pure ethyl acetate is used, no hydrogen is evolved. If the ethyl acetate originally contains alcohol, the quantity of hydrogen evolved is of course greater. (See further, ACETIC ETHERS, p. 15.) Wanklyn also finds that amyl acetate, ethyl butyrate, ethyl valerate, and ethyl benzoate when acted upon by sodium do not yield a trace of gas.

Frankland a. Duppa, in a recent communication to the Royal Society (*Proc. Roy. Soc.* xviii. 228), attribute the difference between their own results and those of Wanklyn to the fact that their experiments were made in open vessels, whereas Wanklyn operated in sealed tubes. They however confirm Wanklyn's observation that sodium dissolves in valeric ether under ordinary pressure without evolution of gas, and suggest that in the case of acetic ether, the two reactions—viz. the one observed by themselves, attended with elimination of hydrogen, the other observed by Wanklyn, unattended by evolution of gas—may go on together, the one or the other predominating according as the experiment is made under the ordinary pressure or in sealed tubes. In corroboration of these views, they point to the recent observation of Cailletet, to the effect that the evolution of hydrogen from zinc and hydrochloric acid, or from water and sodium-amalgam, is gradually diminished and finally stopped under increasing pressure. (See CHEMICAL ACTION, p. 428.) Lastly, they point out that, even in most of Wanklyn's experiments with perfectly pure acetic ether, a certain amount, and sometimes a considerable amount, of hydrogen was evolved. In reply to these observations, Wanklyn (*Chem. News*, 1870, xxi. 113) refers to the explanation which he had previously given of the elimination of hydrogen in this process—namely, that it is due to the action of the sodium on alcohol resulting from a secondary decomposition; he regards the conditions under which Frankland and Duppa's experiments were made—namely, the high temperature (130°) and the great length of time (several days) occupied in the process—as peculiarly favourable to the occurrence of this secondary action. Finally, he observes that potassium dissolves without effervescence in pure acetic ether contained in an open vessel at ordinary atmospheric pressure.

ETHYL in the free state, or **DIETHYL**, $C^4H^{10} = \begin{array}{l}CH^2(CH^3)\\|\\CH^2(CH^3)\end{array}$ or $C\left\{\begin{array}{l}CH^2CH^3\\CH^3\\H^2\end{array}\right.$, is identical with butane, butyl hydride, or tetryl hydride (v. 735), and isomeric with trimethyl-methane or trimethylformene, $C\left\{\begin{array}{l}(CH^3)^3\\H\end{array}\right.$, produced by the action of zinc and water on tertiary butyl iodide (p. 374). These are in fact the only two possible modifications of the saturated hydrocarbon C^4H^{10}, the one having an atom of carbon directly united with three other carbon-atoms, whereas in the other no carbon-atom is associated with more than two others:


Diethyl.


Trimethyl-methane.

According to Schöyen (*Ann. Ch. Pharm.* cxxx. 233), pure ethyl or diethyl is easily obtained by heating a mixture of ethyl iodide and an equal volume of anhydrous ether with thin strips of zinc, in sealed tubes filled to about three-fourths, first to 100°, afterwards to 130°–140°, for several hours. On cooling the tubes in iced water and opening them, the ethyl gas is evolved and may be collected in a gas-holder.

A mixture of ethyl gas and chlorine exposed to diffused daylight yields an oily strong-smelling liquid, consisting chiefly of chlorodiethyl or butyl chloride, $C^4H^9Cl = \begin{array}{l}C^2H^5\\|\\C^2H^4Cl\end{array}$, which may be converted by saponification into primary butyl alcohol (Schöyen, p. 372).

Ethyl gas heated to 100° with excess of bromine in sealed tubes is converted into butylene bromide and hydrobromic acid: $C^4H^{10} + 2Br^2 = C^4H^8Br^2 + 2HBr$ (Carius, *Ann. Ch. Pharm.* cxxvi. 195).

ETHYL, ACETYLINATED, SALTS OF. Acetylinated ethyl, or *Acetethyl*, as its name implies, is ethyl with some of its hydrogen replaced by acetyl, C^2H^3O. Wanklyn attributes such a structure to some compounds derived from acetic ether. Thus the oily liquid obtained by acting on acetic ether with metallic sodium, and subsequently treating the solid product with any dilute acid, is acetate of acetylinated ethyl. Treatment of the same solid product with methyl iodide gives propionate of acetylinated ethyl; similarly, treatment with ethyl iodide gives butyrate of acetylinated ethyl. Another method of obtaining the salts of acetylinated ethyl is by the successive action of acetic ether and an iodide of an alcohol-radicle on ethylate of sodium: thus by acting on ethylate of sodium, first with acetic ether, and then with ethyl iodide, there is produced isocaproate of acetylinated ethyl.

These compounds, which Wanklyn regards as salts of acetylinated ethyl, were originally discovered by Geuther and by Frankland and Duppa, by whom they were looked upon in a totally different light (p. 589).

The following table exhibits the several formulæ assigned to these compounds, together with their specific gravities and boiling points:

Formulæ according to:

Wanklyn.		Frankland and Duppa.	Boiling point.	Specific gravity.
$\left.\begin{matrix}C^2H^4(C^2H^3O)\\C^2H^3O\end{matrix}\right\}O$ Acetate.	$= H(C^2H^3O)^3$ Hydrogen-triacetyl.	$= C^3H^5O.CO^2C^2H^5$ Ethylic Acetone carbonate.	181°	1·030 at 5°
$\left.\begin{matrix}C^2H^4(C^2H^3O)\\C^3H^5O\end{matrix}\right\}O$ Propionate.	$= CH^3(C^2H^3O)^3$ Methyl-triacetyl.	$= C^3H^4(CH^3)O.CO^2C^2H^5$ Ethylic Methacetone carbonate.	187°	1·009 at 6°
$\left.\begin{matrix}C^2H^4(C^2H^3O)\\C^4H^7O\end{matrix}\right\}O$ Butyrate.	$= C^2H^5(C^2H^3O)^3$ Ethyl-triacetyl.	$= C^3H^4(C^2H^5)O.CO^2C^2H^5$ Ethylic Ethacetone-carbonate.	195°	0·998 at 12°
$\left.\begin{matrix}C^2H^4(C^2H^3O)\\\beta C^4H^7O\end{matrix}\right\}O$ Isobutyrate.		$= C^3H^3(CH^3)^2O.CO^2C^2H^5$ Ethylic Dimethacetone carbonate.	184°	0·991 at 16°
$\left.\begin{matrix}C^2H^4(C^2H^3O)\\C^5H^9O\end{matrix}\right\}O$ Isovalerate.	$= C^3H^7(C^2H^3O)^3$ Isopropyl-triacetyl.	$= C^3H^4(C^3H^7)O.CO^2C^2H^5$ Ethylic Isopropacetone carbonate.	201°	0·9805 at 0°
$\left.\begin{matrix}C^2H^4(C^2H^3O)\\C^6H^{11}O\end{matrix}\right\}O$ Isocaproate.		$= C^3H^3(C^2H^5)^2O.CO^2C^2H^5$ Ethylic Diethacetone carbonate.	210°	0·974 at 20°

Geuther's ethyl-diacetic acid is identical with the acetate of acetethyl, and his ethyl-divaleric acid, $C^{12}H^{22}O^3$, with the caprylate, $C^2H^4(C^2H^3O).OC^8H^{15}O$.

The formulæ in the first column afford perhaps the most intelligible explanation of the formation and principal reactions of these compounds. The reactions in question are: 1. Exchange of acetyl for hydrogen by treatment with sodium ethylate, resulting in the formation of a compound ether and a salt of ethylene-sodium: *e.g.*,

$$\underset{\text{Butyrate.}}{\left.\begin{matrix}C^2H^4(C^2H^3O\\C^4H^7O\end{matrix}\right\}O} + \underset{\text{Sodium Ethylate.}}{C^2H^5NaO} = \underset{\text{Ethyl Butyrate.}}{\left.\begin{matrix}C^2H^5\\C^4H^7O\end{matrix}\right\}O} + \underset{\text{Ethylene-sodium acetate.}}{C^2H^4(C^2H^3O)NaO}$$

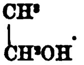
2. Exchange of the two acid-forming radicles for 2 at. hydrogen under the influence of an alkali: *e.g.*,

$$\underset{\text{Butyrate.}}{\left.\begin{matrix}C^2H^4(COCH^3)\\CO(C^3H^7)\end{matrix}\right\}O} + H^2BaO^2 = \underset{\text{Alcohol.}}{\left.\begin{matrix}C^2H^4H\\H\end{matrix}\right\}O} + \underset{\text{Ketone.}}{CO\left\{\begin{matrix}CH^3\\C^3H^7\end{matrix}\right.} + \left.\begin{matrix}CO\\Ba\end{matrix}\right\}O^2.$$

A salt of acetylinated ethyl may obviously be regarded as ethylene half saturated with acetyl and half with acetyl-oxide; as a sort of half ketone and half acetic ether of ethylene.

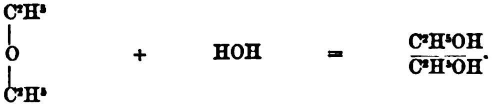
J. A. W.

ETHYL ALCOHOL. $C^2H^6O = C^2H^5OH =$



$$\begin{array}{l} CH^3 \\ | \\ CH^2OH \end{array}.$$

Formation.—Erlenmeyer a. Tscheppe (*Zeitschr. f. Chem.* [2] iv. 343) have obtained alcohol from ether by heating the latter to 150°–180° with water slightly acidulated with sulphuric acid:



$$\begin{array}{c} C^2H^5 \\ | \\ O \\ | \\ C^2H^5 \end{array} \quad + \quad HOH \quad = \quad \frac{C^2H^5OH}{C^2H^5OH}.$$

Linnemann (*Ann. Ch. Pharm.* cxlviii. 249) has produced the same alcohol by reduction of *acetic anhydride* with sodium-amalgam. Acetic anhydride is gradually poured upon an amalgam containing 4 p. c. sodium, the vessel being kept cool, and care being taken that the mass does not harden. When the mixture no longer becomes hot on agitation, but appears dry and dusty, it is agitated with snow, which melts, with considerable reduction of temperature, the amalgam at the same time deliquescing, almost without evolution of gas. Water is then added, together with a little fresh amalgam; the mixture is left to itself for a while, then freed from an oily substance by filtration, and neutralised with potassium carbonate; and the decanted liquid is dehydrated with solid potassium carbonate. The liquid thus obtained is ordinary alcohol. Its formation may be represented by the following equations:

$$\left.\begin{array}{l} C^2H^3O \\ C^2H^3O \end{array}\right\} \quad - \quad O \quad = \quad \left.\begin{array}{l} C^2H^3O \\ C^2H^3O \end{array}\right\}$$

and

$$\left.\begin{array}{l} C^2H^3O \\ C^2H^3O \end{array}\right\} \quad + \quad 3H^2 \quad = \quad 2C^2H^5OH.$$

Reactions.—1. By oxidation with *chromic acid mixture* (p. 150), alcohol is completely converted into acetic acid: $C^2H^6O + O^2 = C^2H^4O^2 + H^2O$ (Chapman a. Thorp). With *potassium permanganate* and dilute sulphuric acid it yields acetic acid and aldehyde; with the permanganate alone, oxalic acid and other products, including only small quantities of aldehyde and acetic acid; with the permanganate in alkaline solution, neither aldehyde nor acetic acid, but either oxalic acid (at ordinary temperatures) or various other acids (at higher temperatures) (Chapman a. Smith, *Chem. Soc. J.* [2] v. 301).

2. Absolute alcohol mixed in a well-cooled retort with 1 mol. *phosphorus trichloride*, is strongly attacked, yielding liquid ethyl-phosphorous chloride, $PCl^2(OC^2H^5)$, which distils at 90°–125°:

$$PCl^3 + C^2H^5OH = HCl + PCl^2(OC^2H^5).$$

Similar reactions take place with butylic and amylic alcohols (Menschutkin, *Ann. Ch. Pharm.* cxxxix. 343).

3. *Phosphorus suphochloride* likewise acts very strongly upon alcohol, producing ethyl chloride and ethyl-sulphoxyphosphoric acid, $(C^2H^5)H^2PSO^3$, an oily, fetid, non-distillable liquid, heavier than water and insoluble therein:

$$PSCl^3 + 3C^2H^5OH = (C^2H^5)H^2PSO^3 + 2C^2H^5Cl + HCl.$$

A small quantity of ethylphosphoric acid is however formed at the same time, with separation of sulphur (Chevrier, *Zeitschr. f. Chem.* [2] v. 413).

4. *Sulphuric chlorhydrate*, $(SO^2)''Cl(OH)$, forms with 1 mol. absolute alcohol, a black tarry mass which in contact with water becomes hot and gives off an irritating gas. With 1 mol. sulphuric chlorhydrate and 2 mol. alcohol, the residue consists of a thick brownish liquid, resolved by water into oily neutral ethyl sulphate, $S(C^2H^5)^2O^4$, and soluble ethyl-sulphuric acid, $S(C^2H^5)HO^4$ (Baumstark, *Ann. Ch. Pharm.* cxl. 75).

5. *Stannic chloride* etherifies alcohol even more readily than sulphuric acid, and may be advantageously substituted for the latter in the preparation of compound ethers. It first unites with the alcohol, forming the compound $2C^2H^6O.SnCl^4$ [or, according to Lewy, $2(C^2H^5Cl.HCl).SnO^2$], which, when in presence of an acid, forms the compound ether; thus with benzoic acid:

$$2C^2H^6O.SnCl^4 + 2C^7H^6O^2 = 2C^7H^5(C^2H^5)O^2 + SnCl^4.2H^2O.$$

The compound $2C^2H^6O.SnCl^4$ is resolved by alkalis into alcohol and stannic oxide; by ethyl alcohol into ethylic ether and hydrated stannic chloride; with methyl or amyl alcohol in like manner it yields mixed ethers:

$$\begin{aligned} 2C^2H^6O.SnCl^4 + 2H^2O &= 2C^2H^6O + SnO^2 + 4HCl \\ 2C^2H^6O.SnCl^4 + 2C^2H^6O &= 2C^4H^{10}O + SnCl^4.2H^2O \\ 2C^2H^6O.SnCl^4 + 2C^5H^{12}O &= 2(C^2H^5)(C^5H^{11})O + SnCl^4.2H^2O \end{aligned}$$

(Girard a. Chapoteaut, *Bull. Soc. Chim.* [2] viii. 349).

6. Dilute alcohol fermented with *syntonin*, or washed meat and chalk from Sens (which contains a peculiar ferment, *Microzyma cretæ*), is converted into caproic acid and hexyl alcohol, with evolution of marsh gas and hydrogen:

$$7C^2H^6O = 2C^6H^{12}O^2 + 2CH^4 + 2H^2 + 3H^2O$$

and

$$7C^2H^6O = C^6H^{12}O^2 + C^6H^{14}O + 2CH^4 + 4H^2O,$$

these two reactions appearing to go on together (Béchamp, *Compt. rend.* lxvii. 558, 560; *Zeitschr. f. Chem.* [2] iv. 702).

Lieben (*Ann. Chim. med.* September 1869, p. 136) has discovered a new and very delicate test for the presence of alcohol, depending upon its conversion into iodoform. The liquid under examination is heated in a test-tube, into which are then introduced a few grains of iodine and a few drops of potash-solution, whereupon, if alcohol is present, a yellow crystalline precipitate of iodoform is produced, immediately or after some time, according to the degree of solution of the liquid. This test is said to be capable of detecting 1 part of alcohol in 12,000 parts of water. For greater certainty, it is best to examine the precipitate with the microscope, iodoform exhibiting the appearance of hexagonal plates or six-rayed stars. The test just described has been successfully applied to the detection of alcohol in urine.

Sodium Alcohol.—Wanklyn finds that the crystalline compound obtained by saturating absolute alcohol with sodium has the composition $C^8H^{23}NaO^4$ or $C^2H^5NaO.3C^2H^6O$, and bears a temperature of 100° without giving off alcohol. It melts completely at 100°, and remains perfectly colourless so long as it is kept from contact with the air; but the slightest access of air turns it brown. The crystals dissolve with some difficulty in ether, more easily in a mixture of ethyl oxide and acetate. When heated above 100° they give off alcohol, and when kept for some time at 200°, give off the whole of their 3 mol. alcohol, leaving absolute sodium ethylate, C^2H^5NaO, as a white amorphous mass, infusible and very light, so that it floats on ether. It is insoluble in ether, turns brown in the air, like the crystals, and may be heated to 275° or even higher, without alteration. Heated to 100°–200° with ethyl acetate, it yields alcohol and ethylene-sodium acetate, isomeric with sodium butyrate. In like manner, with ethyl valerate it yields alcohol and ethylene-sodium valerate, isomeric with sodium œnanthylate (p. 588).

Sodium ethylate unites with *hydrogen sulphide*, forming the body $C^2H^5NaO.SH^2$, which has considerable stability, but breaks up slowly at 100° into alcohol C^2H^6O, and sodium sulphydrate NaHS; and in like manner with 1 mol. *hydrogen chloride*, *acetyl chloride*, *ethyl acetate*, *ethyl valerate*, and *ethyl benzoate*. All these compounds have considerable stability, but when heated to 100° or 150° they decompose, the second for example into sodium chloride and ethyl acetate:

$$C^2H^5NaO.C^2H^3OCl = NaCl + C^2H^5.C^2H^3O^2$$

(*Chem. Soc. J.* [2] vii. 199). For Wanklyn's views of the constitution of these bodies, see ATOMICITY (p. 244); also SODIUM.

Geuther a. Scheitz (*Zeitschr. f. Chem.* [2] iv. 378), by dissolving 1 pt. of sodium in 8 pts. of absolute alcohol, then sealing the tube, quickly separating the mother-liquor from the crystals when cold, and drying these crystals with filter-paper, either immediately or after washing with ether (which however dissolves them in considerable quantity), have obtained crystals containing $C^2H^5NaO.2C^2H^6O$. They dissolve in absolute alcohol even more freely than in ether, and when left over sulphuric acid in a vacuum, give off the whole of the 2 mol. alcohol (57·2 p. c.).

Dry chlorine acts slowly on sodium ethylate mixed to a pulp with absolute alcohol, producing ethyl chloride, sodium chloride, and oxygen, which oxidises a portion of the alcohol to aldehyde and acetic acid:

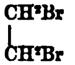
$$C^2H^5NaO + Cl^2 = C^2H^5Cl + NaCl + O.$$

Bromine acts in the same manner, but more quickly. *Iodine* and sodium ethylate yield iodoform (Maly, *Zeitschr. f. Chem.* [2] v. 345).

ETHYL BROMIDE. C^2H^5Br.—Personne (*Compt. rend.* lii. 468) recommends for the preparation of this compound the use of amorphous instead of ordinary phosphorus: 40 grms. amorphous phosphorus are mixed in a retort with 150–160 grms. absolute alcohol, and 100 grms. bromine are slowly poured in through a narrow tube passing through a cork fitted into the neck, the retort being kept cool. The mixture is then distilled into a cooled receiver; the distillate is treated with water; and the ethyl bromide thereby separated is dried over calcium chloride and rectified. Ethyl bromide is also produced by heating amyl bromide with ethyl alcohol; and this reaction, as well as the corresponding one with methyl alcohol, may be made available for obtaining the bromides of ethyl and methyl for the preparation of aniline-green (Hofmann a. Girard, p. 163).

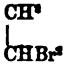
Brominated derivatives of Ethyl bromide are produced by heating ethyl bromide with bromine to 170° in sealed tubes. The product submitted to fractional distillation yields monobromethyl bromide, $C^2H^4Br.Br$, which boils at 110°–112°, has a sp. gr. of 2·135 at 0°, and is isomeric with ethylene bromide, $C^2H^4Br^2$; and dibromethyl bromide, $C^2H^3Br^2.Br$, boiling at 187°, having a sp. gr. of 2·659 at 0°, and identical with monobromethylene bromide, $C^2H^3Br.Br^2$ (Caventou, *Compt. rend.* lii. 1330).

Monobromethyl bromide is probably identical with ethylidene bromide, produced by the action of phosphorus pentachloride on aldehyde (ii. 599); its relation to ethylene bromide is represented by the following formulæ:



$$\begin{array}{l} CH^2Br \\ | \\ CH^2Br \end{array}$$

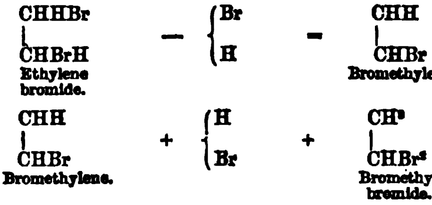
Ethylene bromide.



$$\begin{array}{l} CH^3 \\ | \\ CHBr^2 \end{array}$$

Bromethyl bromide or Ethylidene bromide.

Reboul has observed that monobromethylene heated in sealed tubes with hydrobromic acid yields the latter compound, instead of reproducing ethylene bromide, a result easily accounted for if we suppose that, in the formation of bromethylene from ethylene bromide, the elements of hydrobromic acid are abstracted from both of the semimolecules CH^2Br, and that in the conversion of the bromethylene into bromethyl bromide or ethylidene bromide, the same elements are added on in the reverse order; thus:



$$\begin{array}{l} CHHBr \\ | \\ CHBrH \end{array} - \left\{ \begin{array}{l} Br \\ H \end{array} \right. = \begin{array}{l} CHH \\ | \\ CHBr \end{array}$$

Ethylene bromide. Bromethylene.

$$\begin{array}{l} CHH \\ | \\ CHBr \end{array} + \left\{ \begin{array}{l} H \\ Br \end{array} \right. + \begin{array}{l} CH^3 \\ | \\ CHBr^2 \end{array}$$

Bromethylene. Bromethyl bromide.

According to Caventou, bromethyl bromide treated with alcoholic solution of potassium acetate, yields a small quantity of ethylene diacetate, a result most probably due to the previous conversion of a portion of the bromethyl bromide into the isomeric compound ethylene bromide (*Dictionnaire de Chimie*, i. 1314).

ETHYL CHLORIDE, C^2H^5Cl, is formed: *α*. By the action of chlorine on ethane, C^2H^6 (whether produced from a methyl-compound, *e.g.* by the electrolysis of acetic acid, or from an ethyl-compound, *e.g.* by the action of sulphuric acid on mercuric ethide), the two gases being mixed in the shade and at the temperature of 5° (Schorlemmer, *Compt. rend.* lviii. 703; *Ann. Ch. Pharm.* cxxxv. 234; *Jahresb.* 1864, p. 467).

β. By the action of phosphorus pentachloride on potassium ethylsulphate, sulphuryl chloride being formed at the same time (Naquet, *Dictionnaire de Chimie*, i. 1315):

$$SO^2\left\{ \begin{array}{l} OC^2H^5 \\ OK \end{array} \right. + 2PCl^5 = C^2H^5Cl + SO^2Cl^2 + 2POCl^3 + KCl.$$

Ethyl chloride heated in sealed tubes for five hours to 130° with three or four times its weight of aqueous *hydriodic acid*, sp. gr. 1·9, is for the most part converted into ethyl iodide (Lieben, see p. 437).

Ethyl chloride is absorbed by *sulphuric anhydride*, forming chlorethyl-sulphuric acid, $SO^2\left\{ \begin{array}{l} OC^2H^5 \\ Cl \end{array} \right.$ (R. Williamson, ii. 529; v. 576). This compound has lately been further investigated by Purgold (*Zeitschr. f. Chem.* [2] iv. 669), who, however, makes no reference to Williamson's results. He finds that it boils in a vacuum at 80°–82°, has a sp. gr. of 1·379 at 0°; 1·3556 at 27°; 1·324 at 61°. It is insoluble in water, and when heated with water in sealed tubes, yields ethyl oxide, ethyl chloride, hydrochloric acid, and sulphuric acid; alcohol decomposes it in a similar manner. When ethyl chloride is agitated in a sealed tube with a large excess of sulphuric anhydride, a yellowish acid liquid is formed, which dissolves completely in water and yields a potassium salt having the composition $C^2H^3(OH)\left\{\begin{matrix}SO^2OK\\SO^2OK\end{matrix}\right.$. The same acid is formed in small quantity in the preparation of chlorethylsulphuric acid (Purgold).

Monochlorinated Ethyl Chloride, $C^2H^4Cl.Cl$, is identical with ethylidene chloride, $CH^3—CHCl^2$, having very nearly the same boiling point and specific gravity (ii. 581, 599), and being converted by sodium ethylate and by alcoholic potash under pressure, into vinyl chloride, C^2H^3Cl (Beilstein, *Ann. Ch. Pharm.* cxiii. 110).

Chlorethyl chloride heated to 140° in sealed tubes with a solution of neutral sodium sulphite is converted into sodium chlorethylsulphate:

$$C^2H^4ClSO^3Na \quad \text{or} \quad SO^2\left\{\begin{matrix}OC^2H^4Na\\Cl\end{matrix}\right.$$

(Kind, *Zeitschr. f. Chem.* [2] v. 165). On the other hand, Städel (*ibid.* iv. 272), by heating ethylidene chloride with solution of neutral potassium sulphite in a retort with upright condensing tube, has obtained two acids free from chlorine, viz. ethylidene-sulphuric acid, $CH^3CH\left\{\begin{matrix}SO^3H\\OH\end{matrix}\right.$, and ethylidene-disulphuric acid, $CH^3CH\left\{\begin{matrix}SO^3H\\SO^3H\end{matrix}\right.$.

ETHYL IODIDE, C^2H^5I, is produced by heating the chloride with hydriodic acid in sealed tubes (p. 437). In preparing it by the action of iodine and phosphorus upon alcohol, Personne (*Compt. rend.* lii. 468) recommends the use of amorphous phosphorus: 30 grms. of pulverised amorphous phosphorus and 120 grms. absolute alcohol are introduced into a tubulated retort; 100 grms. of iodine are added in two portions, with an interval of a few minutes, and the mixture is distilled till water no longer separates anything from the liquid which passes over. The product is decolorised with a few drops of potash solution, and washed with water. Rieth a. Beilstein (*Ann. Ch. Pharm.* cxxvi. 250) recommend 10 pts. amorphous phosphorus, 50 pts. alcohol of 90 p. c. (sp. gr. 0·83), and 100 pts. dry iodine, added by small portions, these proportions being founded on the equation:

$$5C^2H^6O + 5I + P = 5C^2H^5I + PH^3O^4 + H^2O.$$

They also recommend that the mixture be left to itself for 24 hours before distillation.

Reactions.—1. Ethyl iodide oxidised with *chromic acid mixture* (p. 150) yields acetic acid, water, and free iodine, $2C^2H^5I + O^3 = 2C^2H^4O^2 + H^2O + I^2$ (Chapman a. Thorp).—2. Heated with *silver powder* to 120°, it yields a combustible gas consisting chiefly of diethyl or butane, C^4H^{10} (Wislicenus, *Zeitschr. f. Chem.* [2] iv. 681).—3. *Bromine* converts it completely in ethyl bromide, without formation of hydrobromic acid (Friedel, *Jahresb.* 1865, p. 491).—4. *Iodine monochloride* gradually added in equivalent quantity converts it into ethyl chloride, with separation of iodine: $C^2H^5I + ICl = I^2 + C^2H^5Cl$ (Geuther, *Ann. Ch. Pharm.* cxxiii. 123).—5. Heated for several hours to 150° with concentrated *hydriodic acid*, it is partly converted into ethane (ethyl hydride), with separation of hydrogen [? iodine: $C^2H^5I + HI = C^2H^6 + I^2$] (Butlerow, *Ann. Ch. Pharm.* cxliv. 36).—6. Heated with *mercuric chloride*, it yields ethyl chloride and mercuric iodide (Oppenheim, *Compt. rend.* lxii. 1085).—7. When ethyl iodide, phosphorus trichloride, and zinc are heated together to 100° for eight or nine hours, the zinc becomes covered with a brown film, and the liquid on cooling deposits crystals of phosphorus di-iodide. The liquid product mixed with water gives off ethane, and deposits a brown substance which contains zinc and gives off hydrogen phosphide when boiled with potash (Chapman a. Smith, *Laboratory*, p. 22).—8. Heated with neutral *potassium sulphite*, it yields ethylsulphite and iodide of potassium:

$$C^2H^5I + KSO^2.OK = KI + C^2H^5.SO^2.OK$$

(Strecker, *Zeitschr. f. Chem.* [2] iv. 213).—9. It is strongly attacked by *sulphuric chlorhydrate*, SO^3HCl, yielding ethylsulphuric acid (Wroblevsky, *Zeitschr. f. Chem.* [2] v. 280).—10. Heated with *amyl alcohol*, it yields hydriodic acid and ethyl-amyl oxide:

$$C^2H^5I + C^5H^{11}.H.O = HI + C^2H^5.C^5H^{11}.O$$

(Friedel a. Crafts, p. 587).

ETHYL OXIDE. $C^4H^{10}O = (C^2H^5)^2O$.—The presence of small quantities of water in common ether may be detected by means of *potassium phosphate*, which is insoluble in anhydrous ether, but dissolves partially in ether containing water, a brown residue being left (Romei, *Zeitschr. anal. Chem.* 1869, p. 390).

Ethyl oxide unites with certain metallic *bromides* and *chlorides*, forming crystallisable compounds, which are decomposed by water and by heat, and decompose carbonates with effervescence (Nicklès, *Compt. rend.* lii. 396; lviii. 537; lx. 479, 800).

Bromo-aluminic Ether, $Al^2Br^6.2C^4H^{10}O$, is obtained by treating ethyl oxide with bromine and aluminium-filings, whereby two layers of liquid are formed, the lower containing the bromo-aluminic ether. This compound is volatile without decomposition, and forms a yellow, very fusible, and deliquescent sublimate, imperfectly soluble in water. An *iodo-aluminic ether* may be obtained in the same manner.

Bromo-antimonious Ether, $SbBr^3.C^4H^{10}O$, formed by the action of bromine on pulverised antimony in contact with ether, is an oily deep yellow liquid, which begins to boil at 91°, giving off bromine, ether, and hydrobromic acid, and leaving a residue of antimonious bromide; part of it however distils without decomposition. Ethyl oxide combines in like manner with *antimonious chloride*, but not with the *iodide*.

Bromo-arsenious Ether, $AsBr^3.C^4H^{10}O$, prepared like the preceding, is more volatile, but decomposes even at ordinary temperatures. Evaporated over sulphuric acid, it leaves a residue of arsenious bromide crystallised in long shining prisms. Volatilises when heated, but is in great part decomposed; is not attacked by zinc. *Arsenious chloride* forms a similar compound.

Bromobismuthic Ether is obtained by direct combination of bismuth bromide with ether under pressure, or by the action of bromine on pulverised bismuth in presence of ether. Over sulphuric acid in a vacuum it crystallises in very deliquescent rhombic prisms containing $BiBr^3.C^4H^{10}O + 2H^2O$. A similar compound is formed with *bismuth chloride*, but not with the *iodide*.

With the *bromides of cadmium* and *zinc*, ethyl oxide forms unstable compounds which fume in the air and dissolve in water, apparently decomposing at the same time; with *ferric bromide* it forms a compound of a deep red colour, decomposible by heat.

Bromomercuric Ether, $HgBr^2.3C^4H^{10}O$, is produced by the action of bromine on mercury under ether; the lower layer of liquid then formed deposits mercuric bromide, and the mother-liquor consists of the ethereal compound.

Chloroboric Ether, $2BCl^3.5C^4H^{10}O + 9aq.(?)$, is a volatile liquid obtained by heating an alcoholic solution of boric acid saturated with hydrochloric acid.

Chloromanganic Ether.—By passing hydrochloric acid gas into a mixture of ether and manganese dioxide in a vessel cooled with ice, Nicklès has obtained a compound to which he assigns the formula $MnCl^4.12C^4H^{10}O + 2aq$. It is a green, very unstable substance, soluble in ether, insoluble in carbon bisulphide, easily reduced by metals, metallic sulphides, &c., yielding manganous chloride.

Chlorothallic Ether, $TlCl^3.C^4H^{10}O.HCl + aq.$ (v. 748). *Chlorostannic Ether*, $SnCl^4.2C^4H^{10}O$ (v. 809).

Substitution-derivatives of Ethyl Oxide.

Dichlorinated Ethyl Oxide, $C^4H^8Cl^2O = \left.\begin{matrix}C^2H^3Cl^2\\C^2H^5\end{matrix}\right\}O$ (formerly called *Monochlorinated ether*, ii. 540).—Lieben a. Bauer (*Ann. Ch. Pharm.* cxxiv. 130. Lieben, *ibid.* cxxxiii. 287; cxli. 236; cxlvi. 180; cl. 87; *Jahresb.* 1864, p. 471; 1866, p. 485; 1867, p. 544).—This compound is best prepared by passing washed and dried chlorine into anhydrous ether cooled to 0° in a flask with upright condensing tube, and after some time (about 10 hours when a kilogram of ether is used) distilling the product in the water-bath, whereby a colourless distillate and a brown residue are obtained. The distillate is again treated in the same manner with chlorine, the product redistilled from the water-bath, and this treatment repeated till the portion volatile at 100° has disappeared. The united dark-coloured residues are then heated in an oil-bath till a thermometer immersed in the vapour rises to 136°; the portion which has passed over is again treated with chlorine; and finally, after another repetition of this treatment, the brown-black residues not volatile at 136° are subjected to fractional distillation. The portion which then distils between 140° and 147° consists for the most part of dichlorinated ethyl oxide. It is a limpid colourless liquid, having an acrid taste, and burning with a green-edged flame; sp. gr. 1·174 at 23°. It dissolves for the most part in water at ordinary temperatures, with evolution of heat and formation of hydrochloric acid, alcohol, and a body which exhibits the reactions of aldehyde.

From the following reactions it appears most probable that the two chlorine-atoms in the molecule of this ether are situated unsymmetrically, as represented by the formula $\left.\begin{matrix}C^2H^3Cl^2\\ C^2H^5\end{matrix}\right\}O$, not symmetrically as in the formula $\left.\begin{matrix}C^2H^4Cl\\ C^2H^4Cl\end{matrix}\right\}O$.

The dichlorinated ether added by drops to an ethereal solution of *zinc-ethyl* cooled to −15°, is converted into ethylochlorinated ethyl oxide, $C^6H^{13}ClO$:

$$2\left[\left.\begin{matrix}C^2H^3Cl^2\\ C^2H^5\end{matrix}\right\}O\right] + Zn(C^2H^5)^2 = ZnCl^2 + 2\left[\left.\begin{matrix}C^2H^3.Cl.C^2H^5\\ C^2H^5\end{matrix}\right\}O\right].$$

This compound is a liquid having a pleasant ethereal odour, and boiling at 137°. Sp. gr. of 0·9735 at 0°. Vapour-density = 69·3, referred to hydrogen as unity (calc. 68·25). It is insoluble in water, but mixes in all proportions with alcohol and ether.

By heating ethylochlorinated ethyl oxide with zinc-ethyl, the remaining atom of chlorine is removed, and diethylated ethyl oxide, $C^8H^{18}O = \left.\begin{matrix}C^2H^3.C^2H^5.C^2H^5\\ C^2H^5\end{matrix}\right\}O$, isomeric with butyl oxide, $(C^4H^9)^2O$, is produced. Dichlorinated ethyl oxide treated with *zinc-methyl* yields methylochlorinated ethyl oxide, $\left.\begin{matrix}C^2H^3.Cl.CH^3\\ C^2H^5\end{matrix}\right\}O$, a colourless aromatic liquid miscible with alcohol and ether, having a sp. gr. of 0·9842 at 0°, and vapour-density = 63 (calc. = 62·25).

Ethylochlorinated ethyl oxide treated with fuming *hydriodic acid* yields, as principal products, ethylated ethyl iodide (or butyl iodide), ethyl iodide, hydrochloric acid, and free iodine, together with butyl chloride and secondary products. The reaction appears to take place as shown by the following equations:

$$\underset{\text{Ethylochlorinated ethyl oxide.}}{\left.\begin{matrix}C^2H^3.Cl.C^2H^5\\ C^2H^5\end{matrix}\right\}O} + 2HI = \underset{\text{Ethylochlorinated ethyl iodide.}}{C^2H^3.Cl.C^2H^5.I} + C^2H^5I + H^2O.$$

$$\underset{\text{Ethylochlorinated ethyl iodide.}}{C^2H^3.Cl.C^2H^5.I} + HI = \underset{\text{Butyl chloride.}}{C^2H^3.Cl.C^2H^5.H} + I^2.$$

$$\underset{\text{Butyl chloride.}}{C^2H^3.Cl.C^2H^5.H} + HI = \underset{\text{Butyl iodide.}}{C^2H^3.I.C^2H^5.H} + HCl.$$

This butyl iodide has the constitution of ethyl-methyl carbinyl iodide, $C\left\{\begin{matrix}C^2H^5\\ CH^3\\ H\\ I\end{matrix}\right.$, and when heated with silver acetate yields the corresponding acetic ether, which, when saponified by potash, yields secondary butyl alcohol or ethyl-methyl carbinol, $C\left\{\begin{matrix}C^2H^5\\ CH^3\\ H\\ OH\end{matrix}\right.$.

Diethylated ethyl oxide treated with *hydriodic acid* yields in like manner diethylated ethyl iodide, $C^2H^3(C^2H^5)^2I = C^6H^{13}I$, from which, by saponification, a secondary or tertiary hexyl alcohol might probably be obtained.

Action of Sodium Alcohol and Alcoholic Potash on Dichlorinated Ethyl Oxide, &c.— Dichlorinated ethyl oxide treated with alcoholic potash, or better with sodium ethylate, is converted into oxethylochlorinated ethyl oxide, $C^6H^{13}ClO^2$:

$$\left.\begin{matrix}C^2H^3Cl^2\\ C^2H^5\end{matrix}\right\}O + C^2H^5ONa = NaCl + \left.\begin{matrix}C^2H^3Cl.C^2H^5O\\ C^2H^5\end{matrix}\right\}O,$$

a limpid colourless liquid having an agreeable refreshing odour, boiling at 157°–158°, heavier than water, and not attacked by aqueous potash, even at the boiling heat.

When 1 mol. dichlorinated ethyl oxide is treated with 2 mol. sodium ethylate, the second atom of chlorine is also, though slowly, replaced by oxethyl, C^2H^5O, yielding dioxethylated ethyl oxide, $\left.\begin{matrix}C^2H^3(C^2H^5O)^2\\ C^2H^5\end{matrix}\right\}O$. This compound is best prepared by heating oxethylochlorinated ethyl oxide with a slight excess of sodium ethylate to 140°–150° for 30 hours, separating the product by water, submitting it to fractional distillation, and heating the portion which goes over between 162° and 171° with sodium. It is a colourless fragrant liquid, not miscible with water, having a sp. gr. of 0·8924 at 21°, and boiling at 168°. Heated with concentrated *hydriodic acid* to 130°, it yields ethyl iodide, alcohol, charcoal, and a small quantity of another iodised compound:

$$\left.\begin{matrix}C^2H^3(C^2H^5O)^2\\ C^2H^5\end{matrix}\right\}O + 2HI = 2C^2H^5I + C^2H^6O + 2H^2O + C^2.$$

Ethylochlorinated ethyl oxide heated to 140° for twenty or thirty hours with *sodium ethylate* or with pasty *alcoholic potash*, is converted into ethyloxethylated ethyl oxide, $C^8H^{18}O^2 = \left.\begin{matrix}C^2H^3.C^2H^5.C^2H^5O\\ C^2H^5\end{matrix}\right\}O$, a liquid having a pleasant ethereal odour, floating on water, and boiling at 147°.

Oxymethyl chlorinated Ethyl oxide, $C^5H^{11}ClO^2 = \left.\begin{matrix}C^2H^3Cl.CH^3O\\ C^2H^5\end{matrix}\right\}O$, produced, like the corresponding ethyl compound, by the action of sodium methylate on dichlorinated ethyl oxide, boils at 137°, and has a sp. gr. of 1·056 at 13·5°.

Action of the Chlorides and Bromides of Phosphorus on Dichlorinated Ethyl Oxide, &c.—Phosphorus tribromide acts upon dichlorinated ethyl oxide at 200° in the manner shown by the equation:

$$3\left[\left.\begin{matrix}C^2H^3Cl^2\\ C^2H^5\end{matrix}\right\}O\right] + 2PBr^3 = 3C^2H^5Br + 3HBr + 6HCl + 6C + P^2O^3.$$

On ethylochlorinated ethyl oxide, phosphorus tribromide acts at 180°, forming phosphorous acid, ethyl bromide, and a chlorobromide, probably consisting of C^4H^8ClBr or $C^2H^3.C^2H^5.ClBr$, which however has not been obtained pure. Methylochlorinated ethyl oxide yields similar products.

Phosphorus pentachloride decomposes dichlorinated ethyl oxide, forming hydrochloric acid and a black liquid containing phosphorus trichloride, together with chlorinated substitution-products of dichlorinated ethyl oxide and their products of decomposition by heat. Ethylochlorinated ethyl oxide reacts with phosphorus pentachloride in a similar manner.

ETHYL SULPHIDE, $(C^2H^5)^2S$, is produced by passing the vapour of sulphurous chloride, SO^2Cl^2, together with a current of carbon dioxide, over zinc-ethyl. On distilling the resulting viscid mass with water, zinc oxide separates, and ethyl sulphide boiling at 91° passes over (F. Gauhe, *Jahresb.* 1867, p. 542).

Ethyl sulphide dissolves in fuming *nitric acid*, with evolution of red vapours, and without formation of sulphuric acid. The acid solution when left to evaporate solidifies to diethylsulphone, $(C^2H^5)^2SO^2$, or sulphuric dioxydiethide, $S^{vi}\left\{\begin{matrix}(C^2H^5)^2\\ O^2\end{matrix}\right.$, which crystallises from hot water or alcohol in long thin tables, melts at 70°, boils at 248°, and is reduced by nascent hydrogen to ethyl sulphide.

Nitric acid of sp. gr. 1·2 dissolves ethyl sulphide without much evolution of gas, forming an acid uncrystallisable liquid, which is converted by potassium ferricyanide and free alkali, by potassium chromate, and by ferric chloride, into several crystallisable compounds whose composition has not yet been determined (A. v. Oefele, *Ann. Ch. Pharm.* cxxvii. 370).

Ethyl sulphide unites directly with chloride, bromide, and iodide of ethyl, forming triethylsulphurous compounds (v. 881) in which the sulphur may be regarded as quadrivalent: *e.g.*,

$$\underset{\text{Ethyl sulphide.}}{(C^2H^5)^2S} + \underset{\text{Ethyl iodide.}}{C^2H^5I} = \underset{\text{Sulphurous triethiodide.}}{S^{iv}\left\{\begin{matrix}(C^2H^5)^3\\ I\end{matrix}\right.}$$

This triethiodide is also formed by heating ethyl sulphide with acetyl iodide in sealed tubes. On dissolving the resulting crystals in water, removing the iodine with silver oxide, neutralising with hydrochloric acid, and adding platinic chloride to the filtrate, crystals of a platinum salt are obtained exhibiting the composition $2[S(C^2H^5)^3Cl].PtCl^4$ (Lukaschewicz, *Zeitschr. f. Chem.* [2] iv. 643).

Ethyl-methyl Sulphide. $C^3H^8S = \left.\begin{matrix}C^2H^5\\ CH^3\end{matrix}\right\}S$ (Carius, *Ann. Ch. Pharm.* cxix. 313; cxx. 61).—Produced by heating ethyl disulphophosphate with 2 vol. anhydrous methyl alcohol to 150° for an hour or two, and distilling the product:

$$\underset{\text{Ethyl-disulphophosphate.}}{\left.\begin{matrix}(PS)'''\\ (C^2H^5)^3\end{matrix}\right\}\begin{matrix}O^2\\ S\end{matrix}} + \underset{\text{Methyl alcohol.}}{\left.\begin{matrix}CH^3\\ H\end{matrix}\right\}O} = \underset{\text{Ethyl-methyl sulphide.}}{\left.\begin{matrix}C^2H^5\\ CH^3\end{matrix}\right\}S} + \underset{\text{Diethyl-sulphophosphoric acid.}}{\left.\begin{matrix}(PS)'''\\ (C^2H^5)^2\\ H\end{matrix}\right\}O^3}$$

Ethyl-methyl sulphide is a colourless liquid having a disagreeable odour, boiling at 58·8°–59·5° (corr.) with the barometer at 757 mm., and having a vapour-density of

2·625 (calc. 2·5–2·6). By oxidation with nitric acid of sp. gr. 1·1, it yields ethylsulphurous acid. Mixed in alcoholic solution with *mercuric chloride*, it forms shining laminæ of the compound $(C^2H^5)(CH^3)S.HgCl^2$. A compound with *mercuric iodide* containing $2(C^2H^5)(CH^3)S.HgI^2$ is produced by boiling a solution of mercuric sulphethylate (mercaptide) in absolute alcohol with methyl iodide. It is a sulphur-yellow crystalline powder, which melts under boiling alcohol, and solidifies on cooling to a mass having the aspect of porcelain. It is sparingly soluble in alcohol, and when boiled with a quantity of that liquid not sufficient to dissolve it, is decomposed, with separation of mercury and mercuric sulphide.

Ethyl-amyl Sulphide. $\left.\begin{matrix}C^2H^5\\C^5H^{11}\end{matrix}\right\}S$ (Carius, *loc. cit.*; Saytzeff, *Ann. Ch. Pharm.* cxxxix. 354; further, *Zeitschr. f. Chem.* [2] vi. 104).—Carius prepares this compound, like the preceding, by the action of amyl alcohol on ethyl disulphophosphate. Saytzeff prepares it by the action of ethyl iodide on sodium-amyl sulphide; also by the action of amyl iodide on a solution of potassium monosulphide in absolute alcohol (potassium-ethyl sulphide), or of amyl chloride on sodium-ethyl sulphide:

$$C^2H^5NaS + C^5H^{11}Cl = NaCl + (C^2H^5)(C^5H^{11})S.$$

On heating the last-mentioned materials together in a sealed tube for 6 to 8 hours, washing the product with water, drying and rectifying, an oily body was obtained, distilling for the most part between 150° and 160°, and after repeated treatment with sodium passing over completely at 157°–159°. It is a colourless liquid having an alliaceous odour, insoluble in water, boiling at 132°–133·5° (corr.) under a pressure of 758 mm. (Carius); at 158° (Saytzeff). Sp. gr. = 0·852 at 0° (Saytzeff). Vapour-density referred to air = 4·4954 (Carius); calc. = 4·5606. By oxidation with nitric acid, it yields, according to Carius, nothing but ethyl-sulphurous acid; according to Saytzeff, on the other hand, the chief product of the oxidation is ethyl-amyl oxysulphide, with only a trace of ethyl-sulphurous acid. The compound of ethyl-amyl sulphide with *mercuric iodide*, $2(C^2H^5)(C^5H^{11})S.HgI^2$, prepared like the corresponding methyl compound, is more easily fusible and more soluble in alcohol than the latter. It is decomposed by heat.

Ethyl-amyl Oxysulphide, $(C^2H^5)(C^5H^{11})SO$, is a viscid liquid insoluble in water, soluble in alcohol and ether, solidifying to a crystalline mass at −16°, and decomposing when distilled. It is not susceptible of further oxidation. Nascent hydrogen reduces it to ethyl-amyl sulphide (Saytzeff).

Ethyl-benzyl Sulphide, $(C^2H^5)(C^7H^7)S$, prepared by the action of ethyl iodide on sodium benzyl-mercaptide, C^7H^7NaS, is a limpid, colourless, very pungent liquid distilling at 214°–216° (Märker, *Ann. Ch. Pharm.* cxl. 86).

Ethyl Bisulphide. $(C^2H^5)^2S^2$.—This compound heated in a sealed tube with 4 mol. ethyl iodide yields sulphurous triethiodide, with separation of iodine:

$$(C^2H^5)^2S^2 + 4C^2H^5I = 2S^{iv}(C^2H^5)^3I + I^2$$

(Saytzeff, *Zeitschr. f. Chem.* [2] vi. 109).

Ethyl Bisulphoxide, $(C^2H^5)^2S^2O^2$, is produced by treating ethyl bisulphide with nitric acid of sp. gr. 1·2 diluted with an equal volume of water. After washing with water and drying over calcium chloride, it forms a colourless transparent liquid, having an alliaceous, somewhat biting odour; it is easily soluble in alcohol and ether, does not crystallise at low temperatures, and is decomposed by boiling even in a vacuum. Strong nitric acid dissolves it without alteration at ordinary temperatures, but oxidises it at the boiling heat to ethylsulphuric acid. By zinc and dilute sulphuric acid it is reduced to bisulphide and ultimately to mercaptan (Lukaschewicz, *Zeitschr. f. Chem.* [2] iv. 641). The same compound appears to have been obtained by Kopp and by Löwig a. Weidmann (*Ann. Ch. Pharm.* xxxv. 343) by the action of nitric acid on mercaptan.

ETHYLACETONE. See KETONES.

ETHYLAMINES. Wanklyn a. Chapman (*Proc. Roy. Soc.* xv. 218) prepare ethylamine by heating equal volumes of ethyl iodide, strong alcohol, and ammonia for half an hour and with constant agitation to a temperature somewhat below 100°. After the free ammonia has been removed by evaporation, the product is distilled with potash; the distillate is received in dilute sulphuric acid; the ammonium sulphate is separated by alcohol; and the alcoholic solution of the remaining sulphate is distilled with a quantity of potash sufficient to liberate about $\frac{2}{10}$ of the bases present. The distillate then contains no base except ethylamine, together with alcohol and water.

By oxidation with chromic acid mixture, ethylamine is converted into nitrogen, water, acetic acid, and aldehyde, without formation of ammonia (Wanklyn a. Chapman, *Chem. Soc. J.* [2] iv. 328).

Hydriodic acid converts ethylamine into ammonia and ethane (Berthelot).

On the conversion of ethylamine into alcohol by the action of nitrous acid, see ALCOHOLS (p. 63).

Ethylamine heated in sealed tubes with *ethyl orthoformate*, $CH(OC^2H^5)^3$, converts that ether into ordinary ethyl formate, $CHO(OC^2H^5)$ (Wichelhaus, *Zeitschr. f. Chem.* [2] v. 284).

Diethylamine. $(C^2H^5)^2HN$.—The hydrochloride of this base distilled with potassium nitrite yields nitrosethylin or nitrosodiethylin, $(C^2H^5)^2(NO)N$ (iv. 114). *Triethylamine hydrochloride* mixed with a moderately concentrated solution of potassium nitrite is not decomposed in the cold, but yields nitrosodiethylin on boiling the mixture till potassium chloride separates out (Geuther, *Zeitschr. f. Chem.* [2] ii. 513). According to Heintz (*ibid.* 571), the triethylamine salt is not decomposed, or but very slightly, in dilute aqueous solution, whereas with the diethylamine salt the decomposition takes place more easily; the reaction may therefore be applied to the separation of di- and tri-ethylamine.

Tetrethylammonium.—On the salts of this base with metallic acids, see vol. v. p. 731.

ETHYLATE OF SODIUM. See ETHYL ALCOHOL (p. 592).

ETHYL-BENZOIC ACID. $C^9H^{10}O^2 = C^6H^4(C^2H^5).CO^2H$ (Kekulé, *Ann. Ch. Pharm.* cxxxvii. 178. Fittig a. König, *ibid.* cxliv. 277. Kekulé a. Thorpe, *Chem. Soc. J.* [2] vii. 366).—This acid, isomeric with xylic acid, was first obtained by Kekulé, by the action of sodium and carbon dioxide on bromethyl-benzene:

$$C^6H^4Br.C^2H^5 + Na^2 + CO^2 = NaBr + C^6H^4(C^2H^5).CO^2Na.$$

Fittig a. König produced it by oxidising diethyl-benzene with boiling dilute nitric acid:

$$C^6H^4(C^2H^5)^2 + O^6 = CO^2 + 2H^2O + C^6H^4(C^2H^5).CO^2H;$$

and Kekulé a. Thorpe have further examined it and demonstrated the identity of the acids obtained by the two processes.

Ethylbenzoic acid crystallises from boiling water in small laminæ, less soluble in water than benzoic acid; from alcohol in small prisms. It melts at 110°-111° and solidifies on cooling to a radio-crystalline mass; melts also when heated with a small quantity of water not sufficient to dissolve it; sublimes without decomposition below its melting point. Easily soluble in ether and in alcohol.

Barium ethyl-benzoate, $(C^9H^9O^2)Ba + H^2O$, crystallises in concentrically united efflorescent laminæ, soluble in 45 pts. of cold water. The *calcium salt* $(C^9H^9O^2)^2Ca + 2H^2O$ crystallises in feathery tufts of needles. The *copper salt* $(C^9H^9O^2)^2Cu$ is a light blue precipitate quite insoluble in water. The *silver salt* $C^9H^9O^2Ag$ is a white precipitate crystallising in needles from hot water (Fittig a. König).

By further oxidation with nitric acid of greater concentration than that used in its preparation, ethyl-benzoic acid is converted into terephthalic acid, $C^6H^4(CO^2H)^2$ (Fittig a. König).

ETHYL-CROTONIC ACID. $C^6H^{10}O^2 = C\left\{\begin{array}{l}C^2H^5\\(C^2H^4)''\\CO^2H\end{array}\right.$.—This acid, isomeric with pyroterebic acid, is produced by decomposition of diethoxalic acid (iv. 273). Frankland a. Duppa (*Chem. Soc. J.* [2] iii. 133) obtain the ethylic ether by treating ethylic diethoxalate with phosphorous chloride:

$$3C^6H^{11}(C^2H^5)O^3 + PCl^3 = 3C^6H^9(C^2H^5)O^2 + PH^3O^3 + 3HCl.$$

Geuther (*Bull. Soc. Chim.* [2] x. 34; *Jahresb.* 1867, p. 456) prepares the acid by heating ethylic diethoxalate with hydrochloric acid to 150°:

$$\underset{\text{Ethylic diethoxalate.}}{3C^6H^{11}(C^2H^5)O^3} + 3HCl + H^2O = \underset{\substack{\text{Ethyl-}\\\text{crotonic acid.}}}{2C^6H^{10}O^2} + \underset{\text{Propione.}}{3C^5H^{10}O} + \underset{\substack{\text{Ethyl}\\\text{chloride.}}}{3C^2H^5Cl}$$

$$+ \underset{\text{Alcohol.}}{3C^2H^6O} + 5CO^2.$$

By treating diethoxalic acid with phosphorus pentachloride, and distilling the product, Geuther obtained an oily liquid which when treated with water yielded hydrochloric and ethylcrotonic acids, and therefore consisted of ethylcrotonic chloride. The diethoxalic acid is first converted by the pentachloride into diethoxalic chloride:

$$C^6H^{12}O^3 + PCl^5 = POCl^3 + HCl + C^6H^{11}O^2Cl;$$

and this chloride is resolved by distillation into water and ethylcrotonic chloride:

$$C^6H^{11}O^2Cl = H^2O + C^6H^9OCl.$$

Ethylcrotonic acid crystallises very easily from fusion in large four-sided prisms having a peculiar odour, recalling those of pyrogallic and benzoic acids. It melts at 39·5° (Frankland a. Duppa); at 41·5° (Geuther); sublimes at ordinary temperatures; dissolves sparingly in water, very easily in alcohol and ether. The aqueous solution reddens litmus and neutralises the strongest bases. Its salts easily give up part of their acid when their solutions are evaporated; the *barium*, *potassium*, and *sodium salts* are soapy. The sparingly soluble *silver salt* $C^6H^9O^2Ag$ crystallises from water in scales which are not much affected by light; the *cupric salt* $(C^6H^9O^2)^2Cu$ is a greenish-blue precipitate; the *lead salt* $(C^6H^9O^2)^2Pb$ is a white precipitate quite insoluble in water. The *ethylic ether* $C^6H^9O^2.C^2H^5$ is a very mobile liquid having a burning taste and pungent odour, recalling that of peppermint oil and that of fungi; it is nearly insoluble in water, mixes in all proportions with alcohol and ether, boils without decomposition at 165°, and has a sp. gr. of 0·9203 at 13°. It does not oxidise in the air, and is not altered by contact with water, but is resolved by boiling with alcoholic potash into alcohol and ethyl-crotonic acid (Frankland a. Duppa).

ETHYL-DIACETIC ACID. $C^6H^{10}O^3$.—This compound, the sodium salt of which is produced by the action of sodium on ethyl acetate, was regarded by Geuther, who discovered it, as diacetic acid, $C^4H^6O^3$ (*i.e.* acetic anhydride), having 1 at. hydrogen replaced by ethyl; and by Wanklyn at first as hydrogen triacetyl, $H(C^2H^3O)^3$, afterwards as the acetate of acetethyl, $C^2H^4(C^2H^3O).OC^2H^3O$ (pp. 16, 588–590). Its methylic ether, $C^7H^{12}O^3$, is the propionate, and its ethylic ether, $C^8H^{14}O^3$, the butyrate of acetethyl. The latter treated with ammonia forms the amides $C^6H^{11}NO^2$ or $C^6H^9(NH^2)O^2$, and $C^8H^{15}NO^2$ or $C^8H^{13}(NH^2)O^2$, the former soluble in water, alcohol, and ether, melting at 90° and subliming in long needles at 100°; the latter forming monoclinic crystals, which melt at 59·5°, dissolve in alcohol and ether, but are insoluble in water (Geuther, *Jahresb.* 1863, p. 324).

ETHYL-DIVALERIC ACID, $C^{12}H^{22}O^3$, or *Caprylate of Acetethyl*, $\left.\begin{matrix}C^2H^4(C^2H^3O)\\ C^8H^{15}O\end{matrix}\right\}O$ (p. 590) (Geuther a. Greiner, *Bull. Soc. Chim.* [2] vi. 218; *Jahresb.* 1865, p. 319. Greiner, *ibid.* viii. 504; *Jahresb.* 1866, p. 320).—This compound, homologous with the preceding, is formed by the action of sodium on ethyl-valerate, together with another body called *divalerylene-divaleric acid*. The crude product is a semifluid mass, which, when mixed with water, separates into an oily liquid, and the aqueous solution of sodium divalerylene divalerate. On removing the oily liquid by agitation with ether, and mixing the aqueous solution with acetic acid, an oil separates which quickly solidifies, and by solution in ether, evaporation, and crystallisation of the residue from warm alcohol, yields crystallisable divalerylene-divaleric acid.

Ethyldivaleric acid is scarcely fluid at ordinary temperatures; it has a yellowish colour, a disagreeable odour of valeric acid, is insoluble in water, soluble in alcohol and ether. Its sodium salt is a yellow resinous mass soluble in alcohol.

Divalerylene-divaleric acid, $C^{20}H^{34}O^3$, crystallises in transparent rhomboïdal plates melting between 125·5° and 128·5° and distilling at 295°. It is insoluble in water, sparingly soluble in cold alcohol, soluble in boiling alcohol and in ether; does not crystallise from fusion, but solidifies to an amorphous mass. Its *barium* salt is uncrystallisable; the *sodium salt* is soluble in water and in alcohol, and is decomposed by carbonic acid. The *ethylic ether*, obtained by the action of ethyl iodide at 180° on the sodium salt, boils between 250° and 280°.

The action of sodium on ethyl valerate likewise gives rise to several other products. (See VALERIC ETHERS.)

ETHYLENE. C^2H^4.—Formed: α. By electrolysis of a concentrated solution of sodium succinate (Kekulé, *Ann. Ch. Pharm.* cxxxi. 79):

$$C^4H^4Na^2O^4 + H^2O = C^2H^4 + 2CO^2 + Na^2O + H^2.$$

β. Together with benzene, by heating cinnamene with hydrogen in sealed tubes (Berthelot, *Jahresb.* 1866, p. 544):

$$C^8H^8 + H^2 = C^2H^4 + C^6H^6.$$

Reactions.—1. Ethylene heated in a glass tube is decomposed somewhat more easily than marsh gas, yielding chiefly ethane, together with small quantities of acetylene and tarry hydrocarbons: $2C^2H^4 = C^2H^6 + C^2H^2$ (Berthelot, *Jahresb.* 1866, p. 518). By passing it through a porcelain tube heated to not very bright redness, and condensing the liquefiable products in a U-tube cooled to a low temperature, Berthelot has obtained benzene, cinnamene, and crystallisable hydrocarbons distilling at and above 200°, probably naphthalene and naphthalene hydride (*ibid.* 1867, p. 332).—2. Heated in a glass tube to dull redness with an equal volume of acetylene, it yields several products, the chief of which is a very volatile liquid consisting of $C^4H^6 = C^2H^4 + C^2H^2$, isomeric or identical with crotonylene (Berthelot, *ibid.* 1866, p. 519).

3. It unites with *hydriodic acid* at ordinary temperatures, and more quickly at 100°, forming ethyl iodide, C^2H^5I (Berthelot, *ibid.* 1867, p. 344).

4. *Sulphuric chlorhydrate*, SO^3HCl, absorbs dry ethylene at ordinary temperatures, with great evolution of heat and formation of hydrochloric acid; and if the action be ultimately assisted by heating to 88°, there remains a brown oil containing isethionic anhydride, $C^2H^4SO^3$, together with another anhydride, $C^2H^4SO^6$, and the corresponding acids. When ethylene is passed for some time into cooled sulphuric chlorhydrate, a pungent non-distillable oil is formed, which is decomposed by water into sulphuric acid, hydrochloric acid, ethyl chloride, and an oil, $C^2H^5SO^2Cl$, having an odour of mustard-oil, and boiling at 154°. This oil, when exposed to the air, forms two layers, the upper containing sulphuric acid and chlorine, the lower consisting of a viscid non-distillable oil, $C^4H^{10}SO^5$, which is converted by water at 100° into isethionic acid. The oil $C^2H^5SO^2Cl$ is converted by dry ammonia into a solid mass of sal-ammoniac, mixed with large deliquescent tabular crystals of the compound $C^2H^7NSO^3$, which is decomposed by potash, yielding ammonia, ethylamine, and ethionic acid (Baumstark, *Zeitschr. f. Chem.* 1867, p. 566).

5. Ethylene oxidised with *chromic acid mixture* (p. 150) is converted into carbon dioxide and water: $C^2H^4 + O^6 = 2CO^2 + 2H^2O$ (Chapman a. Thorp). Heated to 120° with a solution of crystallised *chromic acid* in a small quantity of water, it is oxidised to aldehyde (Berthelot, *Compt. rend.* lxviii. 334).—6. When a solution of *potassium permanganate* is poured into a vessel containing ethylene gas (12 to 14 grms. of the crystallised salt to 1 litre of the gas) the solution becomes colourless, and the ethylene is oxidised to formic and carbonic acids (Truchot, *Compt. rend.* lxiii. 274); but on agitating the gas with a strongly alkaline solution of the permanganate, added by small portions in a well-cooled vessel, oxalic acid is formed, as well as the two products just mentioned: $C^2H^4 + O^4 = C^2H^2O^4 + H^2O$ (Berthelot, *ibid.* lxiv. 35).

Compounds and Derivatives of Ethylene.

Ethylene bromide, $C^2H^4Br^2$, heated with water to 150°-160°, in a sealed tube, is completely resolved into aldehyde (partly changing into aldehyde resin) and hydrobromic acid:

$$C^2H^4Br^2 + H^2O = 2HBr + C^2H^4O.$$

Heated for several hours with 2 or 3 vol. absolute alcohol to 150°-170°, it forms two layers, the upper containing water, aldehyde, and traces of hydrobromic acid, while the lower is a mixture of ethyl bromide, aldehyde, ether, and alcohol. If a larger proportion of alcohol is used, part of the aldehyde is converted into acetal. Monobromethylene bromide heated with water or alcohol yields exactly the same products (Carius, *Ann. Ch. Pharm.* cxxxi. 172).

Ethylene bromide treated with fuming sulphuric acid or sulphuric anhydride, or heated to 100° with sulphuric chlorhydrate, is converted, with evolution of hydrobromic acid, into bromethylsulphuric acid, $C^2H^5BrSO^4$, the barium salt of which, $(C^2H^4BrSO^4)^2Ba$, crystallises in anhydrous shining scales very soluble in water. The *lead salt* $(C^2H^4BrSO^4)^2Pb + 3H^2O$ crystallises in beautiful scales easily soluble in water; it is very unstable, its solution being decomposed by boiling, with formation of lead sulphide, and probably of glycol or of ethylene oxide; perhaps thus:

$$(C^2H^4BrSO^4)^2Pb + 4H^2O = PbSO^4 + 2HBr + H^2SO^4 + 2C^2H^6O^2.$$

The calcium, magnesium, zinc, and copper salts also crystallise very beautifully, but are likewise decomposed on boiling (Wroblevsky, *Zeitschr. f. Chem.* [2] iv. 563; v. 281).

Monobromethylene or Vinyl bromide, C^2H^3Br, heated for several hours with *mercuric acetate*, glacial acetic acid, and water, is decomposed, with formation of mercuric bromide, partial reduction of the mercuric salt to mercurous salt or metallic mercury, and formation of aldehyde and acetic acid (Linnemann, *Ann. Ch. Pharm.* cxliii. 347). According to Saytzeff a. Glinsky (*Zeitschr. f. Chem.* [2] iii. 675), the products of this reaction (at 100°) are acetic acid and a compound of aldehyde with mercurous bromide, which is deposited as a white amorphous precipitate, turning brown in the air, with separation of aldehyde:

$$2C^2H^3Br + 2(C^2H^3O^2)^2Hg'' + 3H^2O = 5C^2H^4O^2 + C^2H^4O.Hg^2Br^2.$$

Bromethylene dissolves in well-cooled *hypochlorous acid*, forming a product very soluble in water, and not volatile without decomposition, which appears to be a mixture of chlorinated and brominated aldehyde. *Chlorethylene* and hypochlorous acid form monochloraldehyde, C^2H^3ClO, a neutral, oily, easily decomposible liquid, converted by atmospheric oxidation into chloracetic acid (Saytzeff a. Glinsky).

Bromethylene Bromide. $C^2H^3Br^3 = C^2H^3Br.Br^2$ (Glöckuer, *Ann. Ch. Pharm. Suppl.* vii. 107).—This compound is most readily prepared by passing vinyl bromide, C^2H^3Br, into bromine: 46 pts. ethylene bromide are added to a solution of 16 pts. potassium hydrate in 80 pts. alcohol cooled to 0°; the cooling mixture is then removed; and the gradually evolved vinyl bromide is passed into 30 pts. of bromine under water. The product, after washing with aqueous potash and distillation, consists of pure bromethylene bromide boiling at 188°.

This compound heated with water in sealed tubes is very slowly attacked; much more readily by alcohol under the same circumstances (at 160°–180°), yielding ethyl bromide, ethyl oxide, hydrogen bromide, and a liquid which boils at 27°, forms a crystalline compound with acid ammonium sulphite, and appears to consist of monobromaldehyde, C^2H^3BrO:

$$C^2H^3Br^3 + C^2H^5.HO = HBr + C^2H^5Br + C^2H^3BrO;$$

the ethyl oxide results from the action of the ethyl bromide on the excess of alcohol used:

$$C^2H^5Br + C^2H^5.HO = HBr + (C^2H^5)^2O.$$

Bromethylene bromide heated to 150° in a sealed tube with barium hydrate in the proportion of $2C^2H^3Br^3$ to BaH^2O^2, yields a mixture of acetylene, C^2H^2, and bromacetylene, C^2HBr. Mixed with potassium hydrate, $(C^2H^3Br^3:KHO)$, dissolved in ten times its weight of alcohol in a flask filled with hydrogen, the mixture being cooled at first by a freezing mixture, but afterwards exposed to the ordinary atmospheric temperature, it gives off bromacetylene with a small quantity of acetylene; and if the flask be connected with two receivers, the first being empty and the second filled with absolute alcohol, the greater part of the bromacetylene dissolves in this liquid, and the first receiver becomes partly filled with a solution of bromacetylene, C^2HBr, and dibromethylene, $C^2H^2Br^2$. Part of the liquid dibromethylene is, however, converted into a solid body of the same composition, first noticed by Sawitsch: this body is not altered by heating with water to 180°.

If in the preceding reaction the air be not completely excluded, monobromacetic acid is formed, together with bromide of potassium or barium; hence it appears that the first product of the action of the alkaline hydrate on bromethylene bromide is monobromaldehyde:

$$C^2H^3Br.Br^2 + H^2O = 2HBr + C^2H^3BrO,$$

this aldehyde being afterwards converted into bromacetic acid by oxidation. Bromacetic acid is also formed when a solution of bromacetylene in absolute alcohol is exposed to the air:

$$C^2HBr + H^2O + O = C^2H^3BrO^2.$$

ETHYLENE CHLORIDE, $C^2H^4Cl^2$, is decomposed by *potassium*, forming potassium chloride and a mixture of ethylene, chlorethylene, and hydrogen gases:

$$8C^2H^4Cl^2 + 7K^2 = 6C^2H^4 + 2C^2H^3Cl + H^2 + 14KCl.$$

If excess of ethylene chloride is used, the chlorethylene remains dissolved therein (Maumené, *Compt. rend.* lxviii. 931).

TRICHLORETHYLENE, C^2HCl^3, is produced by treating carbon trichloride with zinc and sulphuric acid (as in Geuther's process for preparing carbon dichloride, i. 767). It is contained in the portion of the product which boils between 87° and 90°, and, after repeated rectification, is an oily substance smelling like carbon dichloride, and quickly decomposing in contact with the air, with formation of hydrochloric acid (E. Fischer, *Zeitschr. Chem. Pharm.* 1864, p. 268).

CHLOROBROMETHYLENE, C^2H^2ClBr, is formed, together with hydrocyanic acid, by distilling an alcoholic solution of chlorethylene bromide, $C^2H^3Cl.Br^2$, with potassium cyanide. It is a heavy liquid, boiling in contact with water at 55°–58°; its vapour irritates the eyes and has a pungent odour, like that of benzoyl chloride. It is converted partially on standing, completely by repeated distillation with water, into a solid modification (H. Müller, *Chem. Soc. J.* [2] ii. 420).

Ethylene Iodide, $C^2H^4I^2$, is easily obtained in large quantity by saturating a pasty mixture of iodine and absolute alcohol with ethylene gas, agitating, and repeatedly adding fresh portions of iodine; the iodine-solution decanted from the crystals first formed is again mixed with iodine and treated with ethylene. The ethylene iodide, after washing with cold alcohol, is quite pure (Semenoff, *Zeitschr. Ch. Pharm.* 1864, p. 673).

Ethylene iodide heated with *water* in an exhausted tube to 275° for fifteen hours, is decomposed into ethane, carbon dioxide, and free iodine:

$$7C^2H^4I^2 + 4H^2O = 6C^2H^6 + 2CO^2 + 7I^2.$$

The hydrogen liberated from the water by the carbon of the ethylene iodide, ($C^2H^4I^2 + 4H^2O = 6H^2 + 2CO^2 + I^2$), decomposes the ethylene iodide, according to the equation $C^2H^4I^2 + H^2 = C^2H^6 + I^2$ (Berthelot, *Ann. Ch. Phys.* [4] iii. 211).

Ethylene iodide is decomposed by *mercuric chloride* according to the following equations:

$$\begin{aligned}16HgCl^2 + 6C^2H^4I^2 &= 6C^2H^4ClI + 3(2HgCl^2.HgI^2) + 7HgCl^2.\\ &= 6C^2H^4Cl^2 + 5(2HgCl^2.HgI^2) + HgI^2.\\ &= 6C^2H^3Cl^3 + 4(Hg^2Cl^2.HgI^2) + 2Hg^2I^2 + 6HCl.\end{aligned}$$

Decomposition according to equation 1, takes place at ordinary temperatures, the equation then becoming

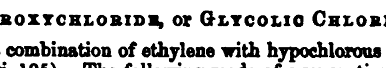
$$3HgCl^2 + 2C^2H^4I^2 = 2C^2H^4ClI + 2HgCl^2.HgI^2.$$

In fact, when an intimate mixture of 1 mol. $C^2H^4I^2$ and 3 mol. $HgCl^2$ is left to itself for some days, it becomes saturated with a red oil consisting of ethylene chloriodide, C^2H^4ClI (ii. 574). The decomposition represented by the second equation takes place when the mixture of $16HgCl^2$ and $6C^2H^4I^2$ is heated to 100°. Ethylene chloride is then obtained, mixed with a certain quantity of the chloriodide, the quantity of which may be diminished by rapid heating, but is always considerable (Maumené, *Compt. rend.* lxviii. 727; *Zeitschr. f. Chem.* [2] v. 366).

Iodethylene, C^2H^3I, heated in alcoholic solution to 100° with silver oxalate, yields silver iodide and a liquid decomposible by water, with formation of oxalic acid, probably an oxalic ether of vinyl alcohol, C^2H^3OH (Semenoff, *Zeitschr. Chem. Pharm.* 1864, p. 673).

Ethylene Chloriodide, C^2H^4ClI, heated to 100°–200° in a sealed flask with 1 mol. moist silver oxide is converted in great part into ethylene alcohol, $C^2H^4(OH)^2$, both the chlorine and the iodine being replaced by hydroxyl. The same results are obtained with 2 mol. silver oxide. The chloriodide heated with water to 160°–220° is also converted into ethylene alcohol, hydrochloric acid, and hydriodic acid, which latter converts part of the ethylene alcohol into iodide. It appears from these results that the chlorine and iodine in the chloriodide are combined with the carbon in the same manner, and that it is not possible to replace one of them with hydroxyl without the other (Maxwell Simpson, *Phil. Mag.* [4] xxxv. 282).

Ethylene Oxide, C^2H^4O, heated to 100° in a sealed tube with acid sodium sulphite is converted into the sodium salt of isethionic acid (Erlenmeyer, *Zeitschr. f. Chem.* [2] iv. 342):



Ethylene Hydroxychloride, or Glycolic Chlorhydrin, $C^2H^4\left\{\begin{matrix}OH\\Cl\end{matrix}\right.$, is produced by direct combination of ethylene with hypochlorous acid, ClOH (Carius, *Ann. Ch. Pharm.* cxxvi. 195). The following mode of preparation is recommended by Butlerow (*ibid.* cxliv. 40). Glass flasks of the capacity of 30 litres or more are filled over water with ethylene gas. To prepare the hypochlorous acid, moist recently precipitated mercuric oxide (10 pts., containing about 4 pts. of the dry oxide, being taken for every litre of ethylene) is mixed with so much ice and water that the mixture shall contain 1 pt. oxide to 15 pts. water, and into this mixture, in a vessel standing in ice-water and in the dark, chlorine gas is slowly passed till the mercuric oxide has nearly disappeared. Half the original quantity of oxide is then added, and the whole is quickly poured into the flasks containing the ethylene, which must then be securely closed. The mixture, after standing for 70 or 80 hours in the dark, is diluted with water and filtered; a quantity of concentrated aqueous sodium hyposulphite is added sufficient to decompose the excess of hypochlorous acid; and the mixture is distilled as long as the distillate exhibits a sweet taste. By saturating this distillate with common salt, agitating with ether, decanting the ethereal solution, and evaporating the ether, the glycolic chlorhydrin is obtained pure.

Glycolic chlorhydrin unites directly with *trimethylamine*, forming the chloride of oxethyl-trimethylammonium, which is identical with the hydrochloride of choline or neurine (Wurtz, p. 448):

$$C^2H^4ClOH + (CH^3)^3N = \left.\begin{matrix}(CH^3)^3\\ C^2H^4OH\end{matrix}\right\}NCl.$$

Glycolic chlorhydrin does not act upon *monosodic glycol* at ordinary temperatures; but on heating the mixture to 130°, ethylene oxide is given off, and on increasing the heat to 250°, a yellow oily liquid passes over, separable by fractional distillation into monoethylenic alcohol (glycol) passing over at 194°–196°, and a small quantity of diethylenic alcohol at 235°–245°. The reaction is:

$$\underset{\substack{\text{Monosodic}\\ \text{glycol}}}{\left.\begin{matrix}C^2H^4\\ Na\\ H\end{matrix}\right\}O^2} + \underset{\substack{\text{Glycolic}\\ \text{chlorhydrin}}}{C^2H^4\left\{\begin{matrix}OH\\ Cl\end{matrix}\right.} = NaCl + \underset{\substack{\text{Diethylenic}\\ \text{alcohol}}}{\left.\begin{matrix}(C^2H^4)^2\\ H^2\end{matrix}\right\}O^3},$$

the greater part of the diethylenic alcohol however splitting up into glycol and ethylene oxide (E. Scheiz, *Zeitschr. f. Chem.* [2] iv. 379). Ethylene monoacetate heated with monosodic glycol to 130°–140° for twelve hours, yields chiefly diethylenic alcohol (R. Mohs, *ibid.* ii. 495; *Jahresb.* 1866, p. 505):

$$\left.\begin{matrix}C^2H^4\\ Na\\ H\end{matrix}\right\}O^2 = \left.\begin{matrix}C^2H^4\\ C^2H^3O\\ H\end{matrix}\right\}O^2 = C^2H^3NaO^2 + \left.\begin{matrix}(C^2H^4)^2\\ H^2\end{matrix}\right\}O^3.$$

ETHYLENE HYDROXYIODIDE, or GLYCOLIC IODHYDRIN, $C^2H^4\left\{\begin{matrix}OH\\ I\end{matrix}\right.$, was first obtained, though not in the pure state, by Maxwell Simpson (ii. 578) by passing hydriodic acid gas into glycol contained in a cooled vessel. According to Butlerow a. Ossokin (*Ann. Ch. Pharm.* cxlv. 257), it is more easily prepared by heating the chlorhydrin, C^2H^4ClOH, with a large excess of finely pulverised potassium iodide to 100° for 24 hours. On treating the resulting mass with the exact quantity of water required to dissolve the chloride and iodide of potassium, a heavy oil separates, coloured black by iodine, from which it may be freed by washing with an alkaline carbonate or sulphite, and if then dried over dehydrated Glauber salt, and distilled in a vacuum, gives off first water, then pure glycolic iodhydrin. This compound is a heavy liquid, not volatile without decomposition, moderately soluble in water, and separable for the most part from the solution by potassium carbonate; it has a peculiar odour, like that of methylene iodide, and a burning sweet taste. With *zinc methyl* (or zinc-ethyl) it reacts in the manner shown by the equations:

$$\left.\begin{matrix}C^2H^4I\\ H\end{matrix}\right\}O + Zn(CH^3)^2 = \left.\begin{matrix}C^2H^4I\\ (ZnCH^3)'\end{matrix}\right\}O + CH^3H$$

$$2\left[\left.\begin{matrix}C^2H^4I\\ (ZnCH^3)'\end{matrix}\right\}O\right] + Zn(CH^3)^2 = 2\left[\left.\begin{matrix}C^2H^4(CH^3)\\ (ZnCH^3)'\end{matrix}\right\}O\right] + ZnI^2.$$

The reaction represented by the first equation is very violent, and is best performed under a layer of benzol. The solid white product treated with water gives off gas and reproduces the iodhydrin:

$$\left.\begin{matrix}C^2H^4I\\ (ZnCH^3)'\end{matrix}\right\}O + 2H^2O = \left.\begin{matrix}C^2H^4I\\ H\end{matrix}\right\}O + CH^4 + ZnH^2O^2.$$

The product of the second reaction, formed under peculiar circumstances, yields when decomposed by water, an alcoholic liquid, which, when zinc-methyl has been used, consists of isopropyl alcohol, C^3H^8O, and in the case of zinc-ethyl, of secondary butyl alcohol or methyl-ethyl carbinol, $C^4H^{10}O$ (Butlerow a. Ossokin).

ETHYLENE NITRITE. $C^2H^4(NO^2)^2$.—Produced by passing dry ethylene gas through liquid nitrogen tetroxide, or by heating the gaseous mixture of the two bodies to 60° or 70°, an oily liquid being formed at the same time; more abundantly and in the pure state by passing ethylene into anhydrous ether, to which liquid nitrogen tetroxide is at the same time added by drops, then cooling the liquid, pressing the crystals which separate between bibulous paper, and drying them over sulphuric acid. The compound is insoluble in water, easily soluble in alcohol or ether, and crystallises in white four-sided prisms or tables which melt at 37·5°, and sublime with partial decomposition at a higher temperature. In a stream of ethylene gas, the compound sublimes at a gentle heat. The fused compound, when cooled to 0°, remains liquid till it is touched with a solid body.

The heavy oily liquid formed, as above mentioned, together with ethylene nitrite, is also very volatile, has a pungent odour, and possesses poisonous properties (Semenoff, *Zeitschr. Ch. Pharm.* 1864, p. 129).

Ethylene Nitroso-nitrate. $C^2H^4N^2O^5 = C^2H^4\left\{\begin{matrix}NO^2\\ NO^3\end{matrix}\right.$—When ethylene gas is continually passed through a cooled mixture of *nitric* and sulphuric acids, an oil collects on the surface, which after washing with water and alkaline carbonate, distillation with aqueous vapour, and dehydration with calcium chloride, exhibits the composition above given. It is a colourless liquid, of sp. gr. 1·472, having an odour spirituous at first, afterwards pungent; its vapour attacks the eyes strongly and produces transient headache. In the dry state it does not volatilise without decomposition, but gives off red fumes even below its boiling point. When distilled with aqueous vapour, it decomposes in great part, with evolution of nitrogen dioxide and trioxide, and formation of oxalic, glycollic, and glyoxylic acids. It is decomposed in like manner by boiling with bases, excepting that the oxidation is less energetic and the proportion of glycollic acid formed is larger. Treated with caustic soda and sodium-amalgam, or with hydriodic acid, it is converted into ethylene alcohol, the whole of the nitrogen being evolved, in the first case as ammonia, in the second chiefly as nitrogen dioxide. The compound $C^2H^4N^2O^5$ is likewise formed by passing ethylene into fuming nitric acid; but a certain portion of the ethylene then undergoes oxidation (Kekulé, *Zeitschr. f. Chem.* [2] v. 601).

Diethylene Bisulphide. $(C^2H^4)^2S^2$ (Husemann, *Ann. Ch. Pharm.* cxxvi. 269; *Jahresb.* 1862, p. 430).—Produced: 1. By heating ethylene trisulphocarbonate (v. 502) with ethylene bromide for a long time (finally to 150°) in a retort fitted with a long upright condenser:

$$C^2H^4.CS^3 + C^2H^4Br^2 = (C^2H^4)^2S^2 + CSBr^2.$$

It collects in the receiver and may be purified by recrystallisation from ether-alcohol.—2. By heating mercuric sulphethylenate (prepared by precipitating an alcoholic solution of ethylene-mercaptan with mercuric chloride) with ethylene bromide to 150° for about six hours, the diethylene bisulphide then subliming:

$$C^2H^4HgS^2 + C^2H^4Br^2 = HgBr^2 + (C^2H^4)^2S^2.$$

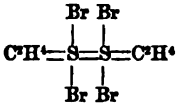
3. The white amorphous ethylene sulphide C^2H^4S (ii. 582), obtained by the action of potassium monosulphide on ethylene chloride (much more easily with the bromide) when heated to 160°–170° for several days with carbon bisulphide, is almost wholly converted into diethylene bisulphide. The same compound heated by itself also yields diethylene bisulphide, together with a black residue and a yellow liquid having a disagreeable odour.

Diethylene bisulphide is slightly soluble in water, easily soluble in hot alcohol, ether, chloroform, benzol, and carbon bisulphide, and crystallises from alcohol in white needles and laminæ grouped like fir-branches; from ether in thick hard monoclinic prisms, mostly combinations of $\infty P . oP . (P\infty)$; it sublimes undecomposed at 56°, melts at 111°, boils at 200°, and has a strong, not altogether unpleasant odour.

Its observed vapour-density 4·28 agrees very nearly with the number 4·156 calculated from the formula $(C^2H^4)^2S^2$, showing that this compound is polymeric with the non-volatile ethylene sulphide C^2H^4S, and is related to it in the same manner as diethylene dioxide $(C^2H^4)^2O^2$ to ethylene oxide C^2H^4O.

Diethylene bisulphide is not attacked by hydrochloric acid, ammonia, or alcoholic potash, and crystallises unaltered from its colourless solution in strong sulphuric acid. Fuming nitric acid dissolves it, forming a blood-red solution which solidifies to a crystalline mass of diethylene oxysulphide. It unites directly with chlorine, bromine, and iodine, but not with cyanogen. In alcoholic solution it forms with mercuric, auric, and platinic chlorides, crystalline compounds containing 1 mol. of the bisulphide to 1 mol. $HgCl^2$ and $PtCl^4$, and 2 mol. $AuCl^3$; these compounds are nearly insoluble in water, but dissolve in hot alcohol, and separate therefrom in microscopic crystals. With silver nitrate in like manner it forms the compound $3(C^2H^4)^2S^2.4AgNO^3$ (polymeric with the ethylidene-compound obtained by Weidenbusch, p. 607), which crystallises in monoclinic prisms or tables, blackens on exposure to light, and decomposes at 140°.

Diethylene Sulphobromide, $(C^2H^4)^2S^2Br^4 = (S^2)^{viii}\left\{\begin{array}{l}(C^2H^4)'' \\ (C^2H^4)'' \\ Br^4\end{array}\right.$, is formed on adding dry bromine to a solution of the bisulphide in anhydrous carbon bisulphide or ether, as a lemon-yellow amorphous precipitate, which decomposes in moist air, more quickly in contact with water or alcohol, into hydrobromic acid (or ethyl bromide) and diethylene oxysulphide. It gives off bromine at 70°, and melts at 96° with copious evolution of hydrobromic acid. This compound may be represented by the structural formula



$$\begin{array}{c} \mathrm{Br}\ \ \mathrm{Br} \\ |\quad\ | \\ C^2H^4{=}S{=}S{=}C^2H^4 \\ |\quad\ | \\ \mathrm{Br}\ \ \mathrm{Br} \end{array}$$

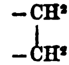
Diethylene Sulphochloride, $(C^2H^4)^2S^2Cl^4$, analogous in structure to the preceding, is deposited on passing dry chlorine into a solution of the bisulphide in carbon bisulphide, as a white amorphous very unstable substance; it is polymeric with Guthrie's ethylene dichlorosulphide (ii. 584).

Diethylene Sulphiodide, $(C^2H^4)^2S^2I^4$, separates on adding iodine to a saturated solution of diethylene bisulphide in ether, alcohol, or carbon bisulphide, in monoclinic needles, iron-black by reflected, red by transmitted light, which are not decomposed by water or by boiling alcohol, but give off iodine at 100° and melt at 132°–133°.

Diethylene Oxysulphide, $(C^2H^4)^2S^2O^2$, is produced, either by decomposing the sulphochloride or sulphobromide with water, or by oxidising diethylene bisulphide with strong nitric acid. It is slightly soluble in alcohol and ether, easily soluble in water, and crystallises in long white prisms or in rhombohedrons, neutral, inodorous, and infusible. Chlorine passed into its solution forms a crystalline precipitate of dichlorethylene oxysulphide, $(C^2H^3Cl)^2S^2O^2$.

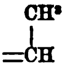
ETHYLIDENE. This diatomic radicle, isomeric with ethylene, has not yet been isolated. Tollens (*Ann. Ch. Pharm.* cxxxvii. 311), by heating ethylidene chloride with sodium to 180°–200° in sealed tubes, obtained a mixture of acetylene, ethylene, chlorethylene, ethane, and probably hydrogen.

The difference of structure between the radicles ethylene and ethylidene is represented by the formulæ:



$$\begin{array}{l} -CH^2 \\ \ \ | \\ -CH^2 \end{array}$$

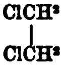
Ethylene.



$$\begin{array}{l} \ CH^3 \\ \ \ | \\ =CH \end{array}$$

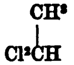
Ethylidene.

In the ethylene-compounds the chlorine, oxygen, &c., are placed symmetrically with regard to the two carbon-atoms, whereas in the ethylidene-compounds their position is unsymmetrical; thus:



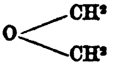
$$\begin{array}{l} ClCH^2 \\ \ \ \ | \\ ClCH^2 \end{array}$$

Ethylene chloride.



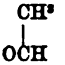
$$\begin{array}{l} \ \ CH^3 \\ \ \ \ | \\ Cl^2CH \end{array}$$

Ethylidene chloride.



$$O\left\langle\begin{array}{l} CH^2 \\ CH^2 \end{array}\right.$$

Ethylene oxide.



$$\begin{array}{l} CH^3 \\ \ \ | \\ OCH \end{array}$$

Aldehyde.

Ethylidene chloride, produced by the action of phosphorus pentachloride on aldehyde, is identical with monochlorethyl chloride, $C^2H^4Cl.Cl$, and ethylidene bromide with monobromethyl bromide (p. 594). Ethylidene chloride heated with aldehyde in sealed tubes yields crotonic aldehyde, C^4H^6O, together with other products (p. 513).

Ethylene in the free state most probably has its carbon-atoms united by two units of affinity: thus $\begin{array}{l} CH^2 \\ \| \\ CH^2 \end{array}$; and under the influence of chlorine, bromine, &c., the bands are loosened as in benzene (p. 196). In ethylidene, on the other hand, this double union of the carbon-atoms is clearly impossible; and consequently ethylidene cannot exist in the free state.

Ethylidene Sulphide. $C^2H^4S = CH^3.CHS$. *Sulphacetyl Hydride* (Weidenbusch, *Ann. Ch. Pharm.* lxvi. 346. Crafts, *Compt. rend.* liv. 1279).—Produced by the action of hydrogen sulphide upon aldehyde. When a current of the gas is passed into a mixture of aldehyde and water, the liquid ultimately deposits a thick limpid oil, which is a compound of ethylidene sulphide and hydrogen sulphide. This compound dried in a vacuum has the composition $6C^2H^4S.H^2S$ (i. 107). It has a sp. gr. of 1·134; is slightly soluble in water, very soluble in alcohol and ether; boils at 180°, decomposing at the same time, and leaving an unctuous mass of ethylidene sulphide. At ordinary temperatures it volatilises rapidly, giving off a very strong and persistent alliaceous odour. Treated with hydrochloric or sulphuric acid, it gives off hydrogen sulphide, and solidifies to a crystalline mass of ethylidene sulphide. The latter is also formed on merely exposing the sulphydric compound to the air.

Ethylidene sulphide is lighter than water, slightly soluble therein, more soluble in alcohol, ether, and carbon bisulphide, and crystallises from the latter in long needle-shaped rhombic prisms of 95°. It distils at 205°, but the boiling point of the fused mass rises with partial decomposition to 260°. As the fused mass cools, the temperature remains stationary for some time at 95°, whilst crystalline laminæ form; then the whole mass becomes soft, and solidifies completely at 70° (Crafts, *Jahresb.* 1862, p. 431). With silver nitrate it forms the compound $3C^2H^4S.2AgNO^3$ (Weidenbusch).

ETHYLIDENE-SULPHURIC or **SULPHETHYLIDENIC ACIDS** (Staedel, *Zeitschr. f. Chem.* [2] iv. 272).—When ethylidene chloride is continuously boiled with solution of neutral potassium sulphite in a flask with upright condenser, two acids are formed which may be separated by the different solubilities of their barium salts. The least soluble of these salts is the *ethylidene-monosulphate* or *monosulphethylidenate*, $C^2H^5SO^4Ba + H^2O$, which forms hard shining transparent crystals, quite different in appearance from the isethionate, with which they are isomeric. The zinc salt of the same acid crystallises in white shining laminæ; the silver salt in needles, the copper salt in thin light green laminæ. The free acid has not been obtained pure.

The more soluble of the two barium salts above mentioned is the *ethylidene-disulphate* or *disulphethylidenate*, $C^2H^4SO^2Ba$, which crystallises with difficulty. All the salts of these two acids, excepting the copper salts, are insoluble in alcohol.

Monosulphethylidenic and Disulphethylidenic acids are related to isethionic and disulphetholic acids respectively, in the same manner as ordinary lactic to paralactic acid, or as isosuccinic to ordinary succinic acid, as may be seen from the following formulæ:

Ethylidene-compounds.	*Ethylene-compounds.*
$CH^3.CH\begin{cases}OH\\COOH\end{cases}$ Lactic.	$\begin{cases}CH^2OH\\CH^2COOH\end{cases}$ Paralactic.
$CH^3.CH\begin{cases}COOH\\COOH\end{cases}$ Isosuccinic.	$\begin{cases}CH^2COOH\\CH^2COOH\end{cases}$ Succinic.
$CH^3,CH\begin{cases}OH\\SO^3H\end{cases}$ Monosulphethylidenic.	$\begin{array}{l}CH^2OH\\ \vert\\ CH^2SO^3H\end{array}$ Isethionic.
$CH^3.CH\begin{cases}SO^3H\\SO^3H\end{cases}$ Disulphethylidenic.	$\begin{array}{l}CH^2SO^3H\\CH^2SO^3H\end{array}$ Disulphetholic.

ETTIDINE. $C^{13}H^{15}N$.—One of the higher bases of the series $C^nH^{2n-11}N$, produced by distilling cinchonine with potassium hydrate (C. Gr. Williams, *Laboratory*, p. 109).

EUGENIA. The red juice of the fruit of the Australian myrtle (*Eugenia australis*) is similar in its properties to that of red grapes. It contains free tartaric acid, cream of tartar, sugar, and a red colouring matter very sensitive to the action of acids and alkalis. By fermentation it yields wine possessing a bouquet. The colouring matter, which is soluble in alcohol and in ether-alcohol, but not in pure ether, is precipitated by lead acetate, decolorised by reducing agents, and recovers its red colour on exposure to the air, just like litmus and the red colouring matter of wine (De Luca a. Ubaldini, *J. Pharm.* [4] iii. 44).

EUGENIC ACID or **EUGENOL.** $C^{10}H^{12}O^2$.—This acid exists in oil of bay (*Laurus nobilis*), together with a hydrocarbon, $C^{10}H^{16}$, boiling at 171°. The eugenic acid from this source boils at 252°, has a sp. gr. of 1·066 at 20°, and a refractive index of 1·5402 for the line D, and 1·5539 for F at 18° (Gladstone, *Chem. Soc. J.* [2] ii. 6). Eugenic acid possessing the same properties (sp. gr. 1·08 at 8°, boiling point 251°) is obtained by the action of potash on oil of pimento (iv. 647).

Eugenic acid distilled with hydriodic acid is resolved into methyl iodide and a residual resinous mass having nearly the composition $C^{9}H^{10}O^{2}$ (Erlenmeyer, *Zeitschr. f. Chem.* [2] ii. 430). By fusion with *potassium hydrate* it yields protocatechuic and acetic acids, the latter being probably due to the decomposition of propionic acid formed in the first instance (Hlasiwetz a. Grabowski, *Ann. Ch. Pharm.* cxxxix. 95):

$$\underset{\text{Eugenic acid.}}{C^{10}H^{12}O^{2}} + O^{7} = \underset{\text{Protocatechuic acid.}}{C^{7}H^{6}O^{4}} + \underset{\text{Acetic acid.}}{C^{2}H^{4}O^{2}} + CO^{2} + H^{2}O.$$

Phosphoric anhydride converts eugenic acid into a resin intermediate in composition between $C^{10}H^{12}O^{2}$ and $C^{10}H^{12}O^{3}$, inodorous, having a bitter and aromatic taste, exhibiting violet-blue dichroism in alcoholic solution; by distillation this resin yields a liquid analogous to creosote, which colours ferric salts green (Hlasiwetz a. Barth, *ibid.* 83).

When eugenic acid is gently heated with *phosphorus trichloride*, a large quantity of hydrochloric acid is evolved, together with a small quantity of gas burning with a green-edged flame; and on distilling off the excess of phosphorous chloride, the residual liquid solidifies at 130° to a porous straw-yellow mass, from which ether extracts eugenic anhydride, $(C^{10}H^{11}O)^{2}O$, in the form of a viscid dark-coloured oil, reconvertible by aqueous potash into eugenic acid. The portion of the product insoluble in ether has the composition of eugenyl-phosphorous acid, $C^{10}H^{13}PO^{4} = \left.\begin{matrix}P'''\\ C^{10}H^{11}O\\ H^{2}\end{matrix}\right\}O^{4}$. Hence the reaction of phosphorous chloride on eugenic acid may be represented by the equation

$$5\left[\left.\begin{matrix}C^{10}H^{11}O\\ H\end{matrix}\right\}O\right] + PCl^{3} = 3HCl + 2(C^{10}H^{11}O)^{2}O + \left.\begin{matrix}P'''\\ C^{10}H^{11}O\\ H^{2}\end{matrix}\right\}O^{3}.$$

Eugenyl-phosphorous acid is an amorphous yellow powder, nearly insoluble in alcohol, and dissolving with difficulty in hot water. The aqueous solution is acid and exhibits the reducing properties of phosphorous acid. Alkalis dissolve it, forming a light brown liquid which quickly becomes darker, and when distilled with sulphuric acid yields eugenic acid. When heated, it swells up, gives off combustible phosphoretted gases, and leaves a bulky cinder, from which water extracts phosphoric acid (Oeser, *Ann. Ch. Pharm.* cxxxi. 277).

EUGETIC ACID. $C^{11}H^{12}O^{4}$.—Formed, as a sodium salt, by passing carbon dioxide into eugenic acid holding sodium in solution. (See Appendix to vol. ii. p. 968.)

EUGLENA SANGUINEA. This plant, which often forms brick-red layers on the surface of ponds, contains a colouring matter insoluble in water, but soluble with garnet-red colour in ether. The solution evaporated on a glass plate leaves an iridescent ring of octohedral crystals, red by transmitted light. The colouring matter is precipitated by alcohol from its ethereal solution, but dissolves in hot alcohol and separates in garnet-red octohedrons, which melt between 70° and 120°, are decolorised by chlorine-water without change of form, and are turned blue by sulphuric acid, but recover their original colour when washed with water. These crystals dissolve very easily in turpentine-oil, and form with potash-ley a blood-red liquid, from which acids separate red drops possessing the properties of the crystals (Wittich, *Chem. Centr.* 1864, p. 576).

EUOSMITE. A fossil resin found in the lignite of Thumsenreuth in the Bavarian Oberpfalz. It occurs sometimes in brownish-yellow pulverulent masses, sometimes in compact lumps having the aspect of pitch. Sp. gr. 1·2–1·5. Has an agreeable odour of rosemary and camphor; melts at 77°; burns with a bright flame emitting an aromatic odour; dissolves completely in alcohol and ether. According to an analysis by Wittstein, it appears to consist of $C^{34}H^{56}O^{2}$ (C. W. Gümbel, *Jahresb.* 1864, p. 867).

EUPHORBONE. $C^{15}H^{22}O$.—A substance obtained from euphorbium (ii. 607), by precipitating the aqueous extract with tannin, triturating the washed flocculent precipitate with white lead, then boiling it with alcohol, distilling off the alcohol, and dissolving the brownish-yellow deposit in a small quantity of boiling alcohol of 70–75 p. c. On cooling it crystallises in nodules, which may be obtained colourless by recrystallisation. It dissolves very easily in ether, benzol, amyl alcohol, chloroform, and acetic acid; is nearly insoluble in water; dissolves in 59 pts. of alcohol (of 87 vol. p. c.) at 17·5°, very abundantly in boiling alcohol; melts between 106° and 116°.

It is neutral, and is not dissolved by acids or bases more abundantly than by water. Nitric acid oxidises it to oxalic acid and a non-crystallisable acid. Strong sulphuric acid dissolves it somewhat sparingly, forming a yellowish-brown solution which is coloured violet by nitric acid and by chlorate or chromate of potassium. It acts as a drastic purgative (Flückiger, *Zeitschr. f. Chem.* [2] iv. 221).

EUSYNCHITE. See VANADATES.

EUTHIOCHRONIC ACID. See Derivatives of Tetrachloroquinone, under QUINONE.

EUXANTHONE. This substance, produced by the decomposition of euxanthic acid, has hitherto been regarded as $C^{20}H^{12}O^6$ or $C^{10}H^6O^3$, its formation being represented by the equation

$$C^{21}H^{12}O^{11} = C^{20}H^{12}O^6 + CO^2 + 3H^2O.$$

But according to Baeyer (*Zeitschr. f. Chem.* v. 569), its analysis is more nearly represented by the formula $C^{13}H^8O^4$, which, moreover, agrees better than the older formula with the substitution-products obtained by Erdmann (ii. 610). When the vapour of euxanthone is passed over heated zinc-dust, a small quantity of a semi-solid hydrocarbon is formed resembling diphenyl. Euxanthone fused with potassium hydrate is first converted, by assumption of water, into euxanthonic acid, and then at a higher temperature into hydroquinone.

Euxanthonic acid, $C^{13}H^{10}O^5$, possesses but feeble acid properties; forms a reddish-yellow precipitate with basic lead acetate; oxidises quickly when dissolved in potash, and is altogether more easily oxidisable than euxanthone. Ferric chloride colours it red, whereas euxanthone is coloured green by the same reagent. When heated, it is resolved into water and euxanthone, which sublimes. The same decomposition takes place also on boiling an aqueous solution of the acid containing ammonia, the euxanthone separating in bulky yellow needles. Euxanthonic acid is much more soluble in water than euxanthone, and crystallises from a hot solution on cooling, in nodules, by evaporation in long yellow needles (Baeyer).

EUXENITE. A specimen of this mineral from Arendal in Norway (sp. gr. 4·96) was found by Chydenius (*Bull. Soc. Chim.* [2] vi. 433) to contain 54·28 Nb^2O^5 and TiO^2, 34·58 YO and EbO, 6·28 ThO, and 2·60 volatile matter (= 97·74).

EVANSITE. A hydrated aluminium phosphate, $3Al^2O^3 . P^2O^5 + 18aq.$, occurring in Hungary as an incrustation in the cavities of brown hæmatite. It is amorphous. kidney-shaped to botryoïdal, colourless or milk-white, sometimes with a tinge of yellow or blue, transparent to translucent. Fracture semi-conchoïdal, shining. Hardness, 3·5 to 4. Sp. gr. (mean), 1·939. Perfectly soluble in acids (D. Forbes, *Phil. Mag.* [4] xxviii. 341).

EVERNIIN. $C^9H^{14}O^7$ (Stude, *Ann. Ch. Pharm.* cxxxi. 241).—A substance related to the sugars, extracted from *Evernia prunastri*. The plant is macerated with cold dilute soda-ley till the liquid acquires a dark green colour; the filtrate is mixed with alcohol; and the brown flocks thereby precipitated are redissolved in water and purified by repeated precipitation and boiling with animal charcoal.

Everniin is an amorphous, yellowish, tasteless powder, which swells up in cold water and dissolves easily in hot water. Its aqueous solution gives with lead acetate and ammonia a precipitate soluble in acetic acid. It is precipitated by a large excess of glacial acetic acid. It prevents the precipitation of lead by sulphydric or sulphuric acid, a property likewise possessed by glycogen, inulin, lichenin, and gum. Everniin is not coloured by iodine. Dilute acids easily convert it into glucose.

A substance closely related to, or perhaps identical with everniin, is obtained from *Borrera ciliaris*.

F

FATS. See GLYCERIDES and OILS.

FAUSERITE. A native magnesio-manganous sulphate, $SO^4Mg^2 . 2SO^4Mn + 16H^2O$, occurring in orthorhombic prisms of 88° 42′, modified by the faces of P, $\infty\breve{P}\infty$, $\infty\breve{P}2$ (= 54° 39′) and $\infty\breve{P}\frac{4}{3}$ (= 107° 50′). Hardness = 2·5 to 2·75; sp. gr. = 1·88. Reddish and yellowish white, or transparent and colourless (Breithaupt, *Jahresb.* 1865, p. 900).

FERBERITE. A variety of wolfram from the Sierra Almagrera in southern Spain, having, according to Liebe (*Jahresb.* 1863, p. 825) and Rammelsberg (*ibid.* p. 854), the composition $4MO . 3WO^3$. The specimen examined by Rammelsberg had a sp. gr. of 7·169 and contained 69·88 p. c. WO^3, 0·16 SnO^2, 25·34 FeO, 3·00 MnO, and 1·62 CaO.

FERMENTATION. The main results of Pasteur's researches on alcoholic fermentation are given in vol. ii. pp. 628–630. According to these researches, it appears that the development of the yeast-plant is an essential part of the process; that the yeast-cells grow both in pure sugar-water and in sugar-water containing albuminous substances; but that in the former case, the whole of the nitrogen which, in the original yeast, was partly present in the soluble form, is found, at the end of the fermentation, to have passed into the insoluble form in the newly formed yeast-cells; whereas in the latter case most of the new yeast-cells are found, at the end of the fermentation, to be filled with soluble nitrogenous and mineral substances, which, when introduced into a fresh quantity of sugar-water, are capable of giving rise to the formation and development of new yeast-cells. Yeast added to pure sugar-water lives, in fact, at the expense of the sugar and of the nitrogenous and mineral substances contained within itself; and in the process of alcoholic fermentation, part of the sugar is assimilated by the yeast in the form of cellulose and fat.

In a subsequent paper (*Bull. Soc. Chim.* 1861, pp. 61, 79), relating to the influence of oxygen on the development of yeast in alcoholic fermentation, Pasteur observes that ready-formed yeast can germinate and grow in a liquid containing sugar and albuminous matters, even when oxygen is completely excluded. The quantity of yeast formed in this case is, however, but small, and the fermentation goes on slowly: nevertheless, a large quantity of sugar disappears (60–80 pts. to 1 pt. of yeast). If the air has access to a large surface, the fermentation goes on quickly, and a much larger quantity of yeast is formed in proportion to the quantity of sugar which disappears. In this case also oxygen is absorbed by the yeast, which grows quickly, but does not act so decidedly as a ferment, inasmuch as only 4 to 10 pts. of sugar disappear for 1 pt. of yeast produced. When the air is excluded, the same yeast again acts as a powerful ferment. Pasteur therefore infers that yeast which acts as a ferment in the absence of air, abstracts oxygen from the sugar, and that upon this deoxidising power its action as a ferment depends. The violent activity of the yeast at the commencement of the fermentation is due to oxygen dissolved in the liquid. In liquids containing albumin (yeast, water, &c.), yeast likewise grows, though sparingly, even if the solution does not contain a trace of sugar, provided there is sufficient access of air. But if the air is excluded, this does not take place, even though the liquid may contain, besides albumin, a nonfermentable sugar, such as milk-sugar. The yeast formed in a liquid not containing sugar possesses all the properties of a ferment, and excites fermentation in a solution of sugar excluded from the air.

According to Béchamp, the mould developed in sugar-water (both microphytes and microzoa) contains a peculiar soluble ferment, which at low temperatures gives rise to the *inversion* of cane-sugar, but loses its activity at 60°–80°. This ferment, called *symase* by Béchamp, does not act on starch or glucosides. Similar ferments are found in the petals of certain flowers, and in mulberry juice. In the action of beer-yeast on cane-sugar, the latter is first converted by the symase into inverted sugar, which is consumed by the yeast and contributes to its growth, and is afterwards eliminated in the form of the compounds which constitute the products of alcoholic fermentation (*Compt. rend.* lviii. 601, 723; lix. 496; *Jahresb.* 1864, pp. 574–578).

On the nature and development of yeast, see further Joly a. Musset (*Compt. rend.* lii. 368; *Jahresb.* 1861, p. 725), Pasteur (*Bull. Soc. Chim.* 1862, p. 66; *Jahresb.* 1862,

p. 473), Millon (*Compt. rend.* lvii. 235; lix. 144; *Jahresb.* 1863, p. 583; 1864, p. 579), Duclaux (*Compt. rend.* lviii. 1114; *Jahresb.* 1864, p. 578).

Liebig, who has always been opposed to the theory which attributes fermentation to the action of living organisms, has renewed his objections to it in a recently published memoir (*Ann. Ch. Pharm.* cliii. 1). He points out that the amount of growth of the yeast-plant in a solution of pure sugar is utterly inadequate to account for the quantity of sugar transformed at the same time into alcohol and carbon dioxide, if the growth of the yeast be regarded as an essential condition of that transformation. In proof of this he quotes one of Pasteur's experiments, in which 9899 milligrams of sugar were fully decomposed by a very small quantity of yeast, and at the end of the fermentation the quantity of the yeast-plant produced was found to be only 152 milligrams, the cellulose in it amounting to less than 30 milligrams. Liebig asks then: Are we to regard the assimilation of 30 milligrams of cellulose as the cause of the conversion of 9899 milligrams of sugar into carbon dioxide and alcohol? Moreover, yeast is capable of inducing the resolution of calcium malate into carbon dioxide and calcium carbonate, acetate, and succinate, and of bringing about a variety of transformations upon various organic substances. All these phenomena are, in Liebig's opinion, most readily explained by regarding fermentation as a purely chemical or physico-chemical process. The breaking up of sugar into carbon dioxide and alcohol he places side by side with the decomposition of anhydrous acetic acid into acetone and carbon dioxide (a change brought about by heat), and with the change of an aqueous solution of cyanogen gas into oxamide, which is brought about by the action of the merest trace of aldehyde. Just as the *vibration* produced by the aldehyde determines the rearrangement of the atoms of cyanogen and water so as to constitute oxamide, so Liebig regards the rearrangement of the atoms of sugar as the result of a vibration produced by the chemical changes which take place in some unstable substance produced by the yeast-plant. The growth of the yeast-plant is, according to this idea, only remotely connected with the process of fermentation. 'It is possible,' he says, 'that the physiological process stands in no other relation to the process of fermentation than that, by means of it, a substance is formed in the living cell, which, by an action peculiar to it—resembling that of emulsin on salicin or amygdalin—determines the decomposition of sugar and other organic molecules. In such a case the physiological action would be necessary for the production of this substance, but would be otherwise unconnected with the fermentation properly so called.'

In harmony with this view, Liebig finds that the 'washings' of yeast (which contain no yeast-plant) have the property of instantly converting cane-sugar into grape-sugar; and he anticipates that other very alterable complex substances, besides products of the yeast-plant, will be found to possess the property of setting up that vibration which rearranges grape-sugar into alcohol and carbon dioxide, and is known as the process of alcoholic fermentation.

Pasteur has extended his researches on the action of ferments to the phenomena of putrefaction and decay (*Compt. rend.* lvi. 734, 1189; *Jahresb.* 1863, p. 579). **Putrefaction** he defines as a kind of fermentation which is induced and maintained by animal ferments of the genus *Vibrio* (the six species of which perhaps also act as peculiar ferments), and in contact with the air is always accompanied by decay or eremacausis. In a putrefying liquid containing air left to itself in closed vessels, infusoria (*Monas crepusculum* and *Bacterium termo*) are first developed, which absorb the oxygen of the air and replace it by carbon dioxide, after which they die, and collect as a precipitate at the bottom of the vessel. After this begins the development of vibrios, if the liquid contains their germs, and at the same time putrefaction is set up. If no such germs are present, or if the oxygen has not been completely absorbed, no putrefaction takes place (in the latter case because the vibrios can live only in an atmosphere free from oxygen). Under all circumstances, however, if the air is excluded, the products of the putrefaction undergo no further alteration. If the putrefiable liquid is freely exposed to the air, the oxygen-consuming infusoria are developed as in the former case, but in a continuous manner; their successive generations cover the surface of the liquid with a film which is continually renewed and completely prevents the access of oxygen to the interior of the liquid. The process then goes on as before, but the products of the putrefaction are completely resolved, under the influence of the superficial layer of infusoria, into water, carbon dioxide, and ammonia. The last phase is therefore a process of decay (in very thin layers of liquid it may take place alone), to which the products of putrefaction, as well as the dead infusoria and vibrios, are subject under the influence of the several species of Bacteria and Mucor. An example of the different results obtained accordingly as the air is admitted or excluded, is afforded by the putrefaction of calcium lactate, which, when the air is excluded, terminates with the formation of calcium butyrate and other products, whereas if the air has access to the liquid, the butyrate likewise ultimately disappears. The putrefaction of solid substances (animal carcases) begins in those parts (such as the surface of the body and the intestinal canal) where vibrios or their germs are present, the activity of the former having hitherto been checked by the normal nutrition of the organs. If no vibrios are present, or if their development is checked (as in a piece of meat wrapped in a cloth soaked in spirit, and placed in a close vessel), true putrefaction or decomposition by vibrios does not take place; but as the solid and liquid constituents of the meat nevertheless react upon each other in a certain way, a change takes place, which with small quantities is indicated by the peculiar odour of game; in larger quantities the phenomena of gangrene are developed. This latter change is regarded by Pasteur as essentially distinct from putrefaction, and as analogous to the ripening of fruits after separation from the plant on which they grow.

With regard to decay or eremacausis, Pasteur adduces a number of experiments which he regards as affording decisive proof that organic substances are not oxidised by perfectly pure air. Aqueous infusion of yeast mixed with sugar and heated to the boiling point was enclosed for three years in a sealed glass flask with twice its volume of previously ignited air, for part of the time at a temperature of 25°–30°. At the end of this time, the liquid was still transparent, and the air in the flask contained 18·1 vol. oxygen, 80·5 vol. nitrogen, and 1·4 carbon dioxide. Urine and milk, whether fresh or previously boiled, exhibited, when similarly treated and kept for the same time, only traces of oxidation; the urine had become somewhat darker and had deposited crystals of uric acid and phosphates; the milk was not curdled and still exhibited alkaline reaction. But when the same liquids were enclosed with air in its ordinary state, the whole of the oxygen of the air was absorbed in a few days, with simultaneous formation of variable quantities of carbon dioxide. Oak sawdust which had been boiled with a small quantity of water absorbed from perfectly pure air only a few cubic centimetres of oxygen in a month; whereas the same quantity moistened but not heated, and left in contact for fourteen days with ordinary air, absorbed nearly 140 c.c. oxygen. The sawdust in this latter case had become coated with a microscopic film of Mycelia and spores of Mucidineæ. These results are regarded by Pasteur as affording decisive proof that the decay or slow combustion of animal and vegetable substances depends essentially, like fermentation and putrefaction, on the influence of certain lower organisms (Mucedineæ, Monads, Bacterias, and Mucors), without whose intervention dead organised matter would be almost indestructible.

J. Lemaire (*Compt. rend.* lvii. 958; *Jahresb.* 1863, p. 582) regards Pasteur's views on fermentation and putrefaction as inadmissible. According to his observations, the most various processes of fermentation may be induced by one and the same ferment, and special ferments have no existence, the development of one or another kind of ferment in a liquid depending on the chemical constitution and the neutral or acid reaction of that liquid; atmospheric dust may, however, exert an essential influence, as affording nutriment for infusoria. In a neutral organic liquid, the decomposition is always begun by animal organisms, the vegetable forms (mycoderms) not appearing till the liquid becomes acid. In acid solutions (fruit-juices) mycoderms are first developed, and subsequently, when the acid reaction has disappeared under their influence, infusoria are produced. Solutions containing only a few thousandths of an organic acid (acetic, tartaric, lactic, malic, &c.) quickly kill infusoria; moreover, carbon dioxide is not essential to the existence of these organisms, and vibrios especially cannot long exist in liquids containing carbonic acid, if excluded from access of oxygen. Infusoria and mycoderms are developed in meat accordingly as it is immersed in pure water or in a solution containing organic acids. Lemaire also finds, contrary to Pasteur, that putrefaction does not take place when oxygen is excluded, and that gangrene is essentially the same process. He distinguishes in the process of putrefaction a stage of fetid odour (*période fétide*), in which he has observed 30 different species of infusoria, and a subsequent stage of purification (*période d'épuration*), in which these infusoria disappear, and in the light are replaced by green matter (*Euglenæ*, *Vorticellæ*, and species of *Protococcus*); this purification process may also take place in the dark, but in that case the green matter is not produced. From further experiments, Lemaire concludes that the unrestricted access of air is essential to the progress and completion of the process of putrefaction. Organic substances (flour and meat) kept in closed vessels with water and a small quantity of air at varying temperatures, exhibited a commencement of putrefaction, but this soon ceased, so that at the end of a year the substances were not found to be much altered. Similar results were obtained with juicy fruits kept in closed vessels filled with air or with charcoal powder. The fruits, however, became uneatable (*Compt. rend.* lix. 696).

For an abstract of various researches on the supposed spontaneous generation of minute organisms, and the diffusion of their germs in the air, see *Jahresb.* 1864, p. 580; 1867, p. 743.

Acetous Fermentation.—See Acetic Acid (p. 6).

Butyrous Fermentation.—The ferment to which this kind of fermentation is due is according to Pasteur (*Compt. rend.* lii. 344) an infusorium. The individuals are small cylindrical stems rounded at the ends, usually straight, and occurring singly or in chains of two, three, or more; their medium thickness is 0·002 mm.; the length of a single stem varies from 0·002 to 0·015 or 0·02 mm. They increase by division, may be sown like beer-yeast, and propagate in any medium adapted to their nutrition, even in a liquid containing only sugar, ammonia, and phosphates, and increase as the butyric fermentation progresses. It is remarkable that these infusoria live and multiply without requiring the smallest quantity of air or oxygen; air indeed kills them. Carbonic acid gas passed into the liquid does not interfere with their life or their reproduction; but on passing air through it for an hour or two, the whole of the animalcules sink to the bottom, and the butyric fermentation ceases altogether. Pasteur has also observed an infusorium which excites the fermentation of calcium tartrate, and, like the true butyric acid ferment, belongs to the vibrios, and is capable of growing without access of oxygen (*Compt. rend.* lvi. 416; *Jahresb.* 1863, p. 382).

In the conversion of calcium lactate into butyrate, carbon dioxide and hydrogen are not evolved in the proportion indicated by the equation $2C^3H^6O^3 = C^4H^8O^2 + 2CO^2 + 2H^2$ (ii. 631). The proportion of hydrogen is always smaller; but the ratio of the two gases varies both in one and the same, and in different fermentations; sometimes even pure carbon dioxide is evolved. Butylic alcohol is probably an ordinary product of the butyrous fermentation. The animalcules which induce this kind of fermentation can develop themselves without any other nutriment than a carbohydrate (such as lactic acid), ammonia, and phosphates (Pasteur, *Bull. Soc. Chim.* 1862, p. 52).

According to Béchamp (*Bull. Soc. Chim.* [2] vi. 484), the function of chalk in lactous and butyrous fermentation is not limited to the neutralisation of the resulting acid, but the chalk is itself capable of acting as a ferment. A mixture of starch-paste and powdered chalk with a few drops of creosote becomes liquid after a few days, soluble starch being formed, with traces of dextrin, and the liquid afterwards passing successively into alcoholic, lactous, and butyrous fermentation. A solution of cane-sugar treated in like manner undergoes the same succession of changes. Now pure precipitated calcium carbonate does not exhibit this reaction in the slightest degree when the air is carefully excluded, and the chalk itself loses the power of exciting fermentation if heated in the moist state to about 300°. Hence Béchamp attributes the action in question to a ferment existing in the chalk, and by microscopic examination he has actually discovered in it extremely small pointed corpuscles having a tremulous motion; these he regards as living organisms, and designates as *Microzyma cretæ*. The chalk with which the above-mentioned experiments were made was taken from a block from the cretaceous formation of Sens. Tertiary fresh-water chalk from Pontil (Hérault) exhibited the same fermentative power. Béchamp is of opinion that the Microzyma is very widely diffused, especially in cultivated soils.

The vibratory corpuscles (pébrine) generated in the silkworm disease also act as a ferment, a solution of cane-sugar containing creosote being converted by prolonged contact with them, partly into inverted sugar, partly into alcohol, acetic acid, and a non-volatile acid, probably lactic acid. These vibratory corpuscles contain cellulose (Béchamp, *Compt. rend.* lxiv. 231; lxv. 42).

Gallous Fermentation.—According to Ph. van Tieghem (*Compt. rend.* lxv. 1091), tannic acid does not decompose either with or without access of air, unless the mycelium of a mucidinea is developed within it. The formation of gallic acid in a solution of tannic acid is especially promoted by the development of the spores of two fungi, *Penicillium glaucum* and *Asperulus niger*, with simultaneous access of air. Under these circumstances, and when the fungus is developed in the interior of the solution, gallic acid is produced (together with small quantities of sugar), amounting in a few days to nearly the theoretical quantity. If, on the other hand, the fungus is developed on the surface as a thick fructifying layer, the tannic acid is completely oxidised, with formation of carbon dioxide, so that, after some days, the solution contains only small quantities of gallic acid and sugar. On the other hand, tannic acid remains quite unaltered, when its solution, freed from dissolved oxygen by exhaustion with the air-pump, is left, either alone or in contact with a large quantity of the mycelium, in bottles filled with carbonic acid.

Influence of Antiseptic Substances on Fermentation and Putrefaction.—According to Béchamp (*Ann. Ch. Phys.* [4] vi. 248), a drop or two of creosote added to 100 c.c. of any liquid is sufficient to arrest the development of the spores of fungi and germs of infusoria, but without interfering with the action of ferments; to kill previously developed organisms, much larger quantities are required. Bucholz found that no fungi or infusoria could be detected in milk mixed with a small quantity of phenol; nevertheless the milk slowly turned sour: hence he infers that the [lactous] fermentation is due, not to the action of living organisms, but to a chemical ferment existing or simultaneously formed in the milk, and acted upon by the phenol less quickly than the organisms (*Jahresb.* 1867, p. 742). According to Naunyn (*ibid.* 1865, p. 606), benzol likewise interferes with the action of yeast on sugar solutions. Pienkowsky (*ibid.* 606) has examined the antiseptic action of a considerable number of salts and of a few acids. Raw meat (50 grms.) impregnated with 10 grms. of either of the following compounds, and left in a cellar for a month, neither underwent putrefaction nor became covered with infusoria or mycoderms: potassium, sodium, ammonium, barium, calcium, or lead acetate; sodium, ammonium, calcium, or stannic chloride; aniline nitrate; phenol; acetic acid; cupric chloride or sulphate; mercuric chloride; potassium dichromate; manganous chloride, zinc chloride, zinc sulphate, ferrous sulphate, potassium sulphite, and lead nitrate. After six months, however, superficial decomposition showed itself, accompanied by development of infusoria and mycoderms, excepting in the samples which were impregnated with the following eleven substances: ammonium acetate, barium acetate, calcium chloride, cupric chloride, mercuric chloride, cupric sulphate, lead acetate, aniline nitrate, phenol, acetic acid, and potassium dichromate. Meat soaked in solution of sodium acetate preserved its agreeable odour, was easily dried, and more easily desalinated than meat preserved with common salt. Sodium and potassium alum, aluminium sulphate, sodium phosphate, strontium and barium nitrates, ammonium and sodium oxalates, barium chloride, sodium sulphite and hyposulphite, ammonium nitrate, potassium chlorate, sodium, potassium, magnesium, and ammonium sulphates, manganous acetate, and arsenious acid, exerted no antiseptic action: meat impregnated with them passed into putrid decomposition, and became covered with fungi or infusoria, even in the course of a week (Pienkowsky). A solution of formic acid or a metallic formate may be kept for six months without exhibiting any development of mycoderms. But if the solution of a metallic formate likewise contains sugar, fungi quickly form in it, part of the formic acid at the same time disappearing. On the other hand, the presence of free formic acid, even to the amount of only 0·1 p. c., is a hindrance to the development of these organisms, whereas in solutions containing from 0·5 to 0·6 p. c. hydrochloric acid, fungi can grow, though not so quickly as in neutral liquids. Formic acid is in this respect a more powerful antiseptic for sugar solutions even than phenol; meat on the other hand keeps longer in water containing phenol than in water containing formic acid, and in the latter longer than in pure water. In water acidulated with formic acid, meat becomes covered with a thick layer of mycoderms (Jodin, *Compt. rend.* lxi. 1179).

According to Severi (*Med.-chem. Unters.* i. 257; *Zeitschr. f. Chem.* [2] iv. 285), alcoholic fermentation is not retarded by pepsin, either alone or in presence of free hydrochloric acid; but natural gastric juice in large quantity arrests the process, and in smaller quantity retards it, this action being exerted on the ferment, not on the fermentable substance. Lactous fermentation is neither arrested nor retarded by pepsin (either alone or with hydrochloric acid) or by natural gastric juice. Putrefactive fermentation, on the contrary, is arrested by natural gastric juice, although the animalcules which Pasteur regards as the exciting cause of this change continue to exist in full health and vigour.

On Fermentation in general, see also Williamson (*Chem. News*, xxii. 234, 247, 258, 268, 292, 304, 316; xxiii. 18, 27, 66, 90, 102, 114); Weinberg (*Bäyerisches Industrie- und Gewerbeblatt*, August 1870; *Chem. News*, xxii. 263). On the Germ-theory of Fermentation: Sansom (*Chem. News*, xxii. 241, 254). On Fungi and Fermentation: J. Bell (*Chem. Soc. J.* [2] viii. 387). On Organic Matter in Water: Heisch (*ibid.* viii. 371). On the Development of Fungi in Potable Water: Frankland (*ibid.* ix. 66). On the Carbonic and Alcoholic Fermentation of Sodium Acetate and Ammonium Oxalate: Béchamp (*Compt. rend.* July 4, 1870; *Chem. News*, xxii. 34).

FERREIRA. The resin of *Ferreira spectabilis*, a leguminous plant growing in Brazil, contains an alkaloïd which has been examined by Gintl (*Zeitschr. f. Chem.* [2] v. 284), who regards it as a distinct body, and calls it *angeline* (the pharmaceutical name of the resin being *Resina d'angelim pedra*). The base appears however to be identical with ratanhine (v. 77).

FERROTANTALATES. See TANTALATES.

FERULIC ACID. $C^{10}H^{10}O^4$ (Hlasiwetz a. Barth, *Ann. Ch. Pharm.* cxxxviii. 61; *Jahresb.* 1866, p. 627).—An acid existing in asafœtida, and obtained by precipitating the alcoholic tincture of the resin with an alcoholic solution of neutral lead acetate; freeing the light yellow precipitate as completely as possible from adhering resin by repeated washing with alcohol, and pressure; and decomposing it, suspended in water, with dilute sulphuric acid. The filtered liquid duly concentrated, yields crystals of crude ferulic acid, which when purified by recrystallisation from alcohol, and then from boiling water, form long colourless four-sided needles belonging to the rhombic system. Ferulic acid is tasteless; has an acid reaction; dissolves easily in cold alcohol, not very readily in ether; is nearly insoluble in cold, but very soluble in boiling water; dissolves very easily and with yellow colour in alkalis. The aqueous solution is precipitated by lead acetate and ferric chloride; the ammoniacal solution forms with silver nitrate an egg-yellow precipitate, quickly becoming darker when exposed to light. Strong sulphuric acid dissolves the crystals with yellow, or when warm with brownish-red colour, and the solution exhibits a green fluorescence, which disappears on dilution with water. The acid melts at 153°–154°, and solidifies in the crystalline form.

Ferulic acid is related to eugenic acid, $C^{10}H^{12}O^2$, in the same manner as oxalic acid to acetic acid, and, like eugenic acid, is resolved by fusion with potash into protocatechuic acid, acetic acid, and carbon dioxide, together with a small quantity of oxalic acid:

$$\underset{\text{Ferulic acid.}}{C^{10}H^{10}O^4} + O^4 = \underset{\text{Protocatechuic acid.}}{C^7H^6O^4} + \underset{\text{Acetic acid.}}{C^2H^4O^2} + CO^2.$$

$$\underset{\text{Eugenic acid.}}{C^{10}H^{12}O^2} + O^7 = C^7H^6O^4 + C^2H^4O^2 + CO^2 + H^2O.$$

The acetic acid may be supposed to arise in the first case as a secondary product from malonic acid, and in the second from propionic acid.

Ferulic acid is monobasic. Its *ammonium salt*, $C^{10}H^9O^4(NH^4) + H^2O$, is obtained by spontaneous evaporation in laminar crystals, which give off part of their ammonia at 100°. The *potassium salt* $C^{10}H^9O^4K$ is straw-yellow, deliquescent, and sparingly soluble in alcohol. The *silver salt* $C^{10}H^9O^4Ag$ is a lemon-coloured precipitate, sometimes turning grey.

FEUILLEA. The seeds of *Feuillæa cordifolia*, a Brazilian climbing plant, contain in 4,000 pts.: 1301·5 pts. of a drying fatty oil, 95·5 feuillin, a brownish, uncrystallisable, bitter substance precipitable by basic lead acetate and tannin, 2·1 of a substance crystallising in colourless plates, 57·0 crystallisable fatty acid, 62·0 red resin, 20·4 brown resin, 22·1 gummy substance and iron-greening tannin, and 10·7 glucose (Peckolt, *Arch. Pharm.* [2] cix. 212).

FIBRIN. See PROTEIDS.

FIBROÏN. See SILK.

FILICIC ACID. This acid, discovered by Luck in the root of *Aspidium Filix mas* (ii. 645), has, according to Grabowski (*Ann. Ch. Pharm.* cxliii. 279), the composition $C^{14}H^{18}O^5$. When heated with 4 pts. potassium hydrate and a little water till the mass begins to melt and turn red-brown, it yields as chief products butyric acid and phloroglucin. If, on the other hand, the solution of the acid in strong caustic potash be evaporated only till it becomes pasty, and the mass be then supersaturated with sulphuric acid and treated with ether, the ethereal solution is found to contain, together with phloroglucin, another crystallisable, slightly soluble substance, $C^{10}H^{12}O^4$, which may be regarded as monobutyryl-phloroglucin, $C^6H^5(C^4H^7O)O^3$. Filicic acid has therefore the composition of dibutyryl-phloroglucin, and its decomposition by potash may be represented by the equation

$$\underset{\text{Filicic acid.}}{C^6H^4(C^4H^7O)^2O^3} + 2H^2O = \underset{\text{Butyric acid.}}{2(C^4H^7O)HO} + \underset{\text{Phloroglucin.}}{C^6H^6O^3}$$

Phloroglucin treated with butyryl chloride yields, however, not filicic acid, but an oily substance which crystallises only after long standing, is insoluble in water and in alkalis, but soluble in alcohol and ether (Grabowski).

FILITANNIC ACID and **FILIX-RED** (G. Malin, *Ann. Ch. Pharm.* cxliii. 276).—The aqueous decoction of the root of *Aspidium Filix mas* yields to ether a small quantity of brown greasy resin, and then forms with neutral and basic lead acetate, precipitates containing filitannic acid, which, when separated by decomposing the washed precipitates with hydrogen sulphide, and evaporating the filtrate, forms a brownish extract, purifiable by partial precipitation with neutral lead acetate and decomposition of the lighter portion of the precipitate. It is very much like cinchona-tannic acid; hygroscopic; forms a somewhat turbid solution; is sparingly dissolved by strong alcohol, more freely by ordinary spirit; forms with ferric chloride an olive-green solution, turning violet on addition of sodium carbonate; reduces alkaline cupric solutions; and is precipitated by gelatin. On boiling it with dilute sulphuric acid, dark brick-red flocks of filix-red, $C^{26}H^{18}O^{12}$, are deposited, whilst an uncrystallisable sugar, $C^6H^{12}O^6$, remains in solution. Filix-red, perhaps identical with Luck's tannaspidic acid, is resolved by oxidation with potassium hydrate into protocatechuic acid and phloroglucin.

FILTRATION. Bunsen has contrived a method of filtering under pressure, by which the time occupied in washing precipitates, and the quantity of water required for the purpose, are very greatly reduced. The neck of the funnel containing the filter is passed through the caoutchouc stopper of a wide-mouthed flask of thick glass, and through the same stopper there also passes a bent tube connected with a glass water-pump constructed on the principle of Sprengel's mercury-pump; any other exhausting apparatus might, however, be used. By this means a partial vacuum is made within the flask, and the pressure of the external air on the water in the funnel forces it rapidly through the filter. To prevent the paper filter from being broken by the pressure, it is placed within a funnel of thin platinum foil, made to fit exactly the inside of the glass funnel. A filter thus supported will bear the pressure of an atmosphere without tearing. For filtering liquids which contain corroding gases or vapours, a cylindrical tube having a conical lower termination is used instead of the funnel, a disc of *artificial* pumice (such as is used for polishing), 1 or 2 mm. thick, being placed in the conical neck and fixed water-tight by means of long-fibred flexible asbestos. For details and figures of the apparatus, see the original memoir (*Ann. Ch. Pharm.* cxlviii. 269; also *Zeitschr. f. Chem.* [2] v. 118; *Chemical News*, 1869, xxi. 128).

FLAME. See COMBUSTION.

FLUORHYDRIC ACID, HYDROFLUORIC ACID, or **HYDROGEN FLUORIDE.** This acid, both in the anhydrous state and in aqueous solution, has recently been submitted to very careful examination by G. Gore (*Phil. Trans.* 1869, p. 173; *Chem. Soc. J.* [2] vii. 368; abstr. *Proc. Roy. Soc.* xvii. 256; *Chem. News*, 1869, p. 74).

The anhydrous acid, HF, was prepared by heating dry hydrogen-potassium fluoride to redness in a suitable platinum apparatus. It is a highly dangerous substance, requiring the most extreme care in its manipulation. At ordinary temperatures it is a perfectly colourless, transparent, mobile liquid, and has a sp. gr. of 0·9879 at 12·8°. It is extremely volatile, boils at 19·4°, fumes densely at ordinary temperatures, and greedily absorbs water from the air. Its vapour-tension at 15° is equal to about 7·58 pounds per square inch. On loosening the lid of a bottle containing it at that temperature, the acid vapour is expelled in a jet like steam from a boiler; it may however be perfectly retained in a platinum bottle having a flanged mouth, with a platinum plate secured by clamp-screws and a washer of paraffin. It does not solidify at 34·5°. The gaseous acid does not attack glass, even when left in contact with it for weeks, provided all moisture be excluded. The acid prepared as above was inferred to be free from oxygen: (1) because the double fluoride from which it was prepared, when fused and electrolysed with platinum poles, evolved abundance of inflammable gas at the negative pole, but no gas at the positive pole, although oxides are decomposed by electrolysis before fluorides; (2) because in the electrolysis of the acid with platinum poles, no odour of ozone was evolved, whereas the aqueous acid of various strengths evolves this odour very strongly where electrolysed; and (3) because the acid obtained by heating pure silver fluoride in dry hydrogen exhibited the same properties as that prepared from the hydropotassic fluoride.

Careful determinations of the molecular volume of the acid prepared by heating silver fluoride in hydrogen showed that it is analogous in constitution to hydrochloric acid, not to water, the results indicating that one volume of hydrogen in uniting with fluorine produces two volumes of gas, just as it does in uniting with chlorine.

Numerous experiments were made to electrolyse the anhydrous acid with positive poles of gas-carbon, charcoal of lignum vitæ, and many other kinds of wood, also of palladium, platinum, and gold. The gas-carbon disintegrated rapidly; all the kinds of charcoal flew to pieces quickly; the palladium, gold, and platinum poles were corroded without evolution of gas. With platinum as the positive pole, the acid conducted much more readily than pure water; but with gold it conducted scarcely at all.

Anhydrous hydrofluoric acid scarcely exerts any action on the metalloïds or the noble metals, and even the other metals in the finely divided state do not eliminate hydrogen from it at temperatures between 0° and 20°. Potassium and sodium react with it as with water. With strong hydrochloric acid it produces an active effervescence. Basic oxides unite readily with it, some of them dissolving; on peroxides it has no effect. Some nitrates are not attacked by it, while others (lead, barium, potassium) are decomposed. Fluorides for the most part remain unaltered, but those of the alkali-metals and thallium produce various degrees of chemical action, those of ammonium, potassium, and rubidium uniting powerfully with the acid. Numerous chlorides were also unaffected, but the pentachlorides of phosphorus and antimony, titanic chloride, and the chlorides of the alkali-metals and alkaline-earth-metals, were decomposed with strong action, and generally with effervescence. The chlorates of potassium and sodium were also decomposed, with evolution of chloric acid. The bromides of the alkaline-earth and alkali metals behaved like the chlorides. Potassium bromate rapidly evolved bromine. Numerous iodides remained unaffected, but those of the alkaline-earth and alkali metals were strongly decomposed, in some cases with liberation of iodine. The anhydrous acid decomposes all carbonates with effervescence, and those of the alkaline-earth and alkali metals with violent action. Alkaline borates also produce very violent action. Silico-fluorides of alkali-metal dissolve with effervescence. Sulphides remain unchanged, except those of the alkaline-earth and alkali metals, which rapidly eliminate hydrogen sulphide. Acid sodium sulphite dissolves with effervescence. Sulphates are variously affected. The acid chromates of the alkali-metals dissolve, with violent action, to blood-red liquids, with evolution of chromium fluoride. Potassium cyanide is violently decomposed, with evolution of hydrogen cyanide. Solid organic bodies immersed in the acid are for the most part quickly disintegrated. Gutta-percha, caoutchouc, and numerous gums and resins dissolve to red liquids. Gun-cotton, silk, paper, cotton-wool, calico, gelatin, and parchment are instantly converted into glutinous substances and generally dissolved. Pine-wood is instantly blackened. Sponge is but little changed. The anhydrous acid mixes with wood-spirit, alcohol, ether, but not with benzol; with oil of turpentine it explodes, forming a blood-red liquid.

Aqueous Hydrofluoric Acid.—The commercial aqueous acid is often very impure; but a pure acid may be prepared from it by passing an excess of hydrogen sulphide through the liquid, neutralising the sulphuric and silico-fluoric acids present with potassium carbonate, decanting from the resulting precipitate, removing the excess of hydrogen sulphide with silver carbonate, filtering, distilling the filtrate from a leaden retort connected with a platinum condenser, and finally rectifying.

A very small quantity of hydrofluoric acid lowers the freezing point of water very considerably. When the aqueous acid was electrolysed with platinum for the positive pole, ozone was evolved, and with acid of 30 p. c. (not with that of 10 p. c.) the platinum was attacked.

The chemico-electric series of metals, &c., in acid of 30 p. c. is as follows: zinc, magnesium, aluminium, thallium, indium, cadmium, tin, lead, silicon, iron, nickel, cobalt, antimony, bismuth, mercury, silver, copper, arsenic, osmium, ruthenium, gas-carbon, platinum, rhodium, palladium, tellurium, osmiridium, gold, iridium.

FLUORINE. According to Prat (*Compt. rend.* lxiv. 345, 511; *Jahresb.* 1867, p. 175), the ordinary metallic fluorides are oxyfluorides, fluor-spar, for example, having the composition $CaFlO$ (the atomic weight of fluorine being 29·6); and by heating an ordinary fluoride (oxyfluoride) with potassium chlorate or perchlorate, a mixture of oxygen and fluorine is evolved, from which the fluorine may be removed by metallic silver. By passing the same gaseous mixture over heated baryta, the oxygen is said to be absorbed and pure fluorine left. Fluorine thus obtained is described by Prat as a gas heavier than air, nearly colourless, fuming in the air, and smelling like chlorine; combining in diffused daylight with hydrogen, decomposing water, hydrochloric acid, bromides, and iodides at ordinary temperatures, bleaching indigo and litmus, uniting with bromine, silicon, and most metals. By mixing dilute aqueous hydrofluoric acid with aqueous hypochlorous acid, Prat obtained a gas which he regarded as a compound of chlorine and fluorine; it was darker than chlorine, and formed with silver a mixture of silver chloride and fluoride.

P. Cillis, however, in repeating Prat's experiments, finds that a mixture of calcium fluoride and potassium chlorate yields by ignition nothing but pure oxygen, which exerts no action on metallic silver, and that this oxygen is derived solely from the chlorate, the fluor-spar remaining unaltered, and the residue after washing with water exhibiting exactly the weight of the original fluoride. Hence he concludes that Prat's statements are erroneous, and that his supposed fluorine has no existence (*Zeitschr. f. Chem.* [2] iv. 660).

Estimation of Fluorine.—Fresenius has described a modification of Wohler's method of estimating fluorine, by the quantity of silicon fluoride evolved on heating a fluoride with sulphuric acid and silica, which consists in determining the quantity of silicon thus evolved by the increase in weight of an absorption apparatus containing, in different parts, pumice moistened with water, soda-lime, and fused calcium chloride (*Zeitschr. anal. Chem.* v. 190; *Jahresb.* 1866, p. 1791).

For Kobell and Zalesky's methods of estimating fluorine in phosphates by the quantity of silica which it can remove from glass when evolved in contact therewith, see *Bull. Soc. Chim.* [2] iii. 70; *Zeitschr. anal. Chem.* v. 205; *Jahresb.* 1864, p. 696; 1866, p. 792).

FORMAMIDE, $CH^3NO = \left.\begin{matrix}CHO\\ H^2\end{matrix}\right\}N$, first obtained by Hofmann (ii. 681) by heating ethyl formate with dry ammonia, is likewise produced: α. By heating a dry mixture of 2 pts. dry ammonium formate and 1 pt. urea to 140°, as long as ammonium carbonate is given off (Berend, *Ann. Ch. Pharm.* cxxviii. 355).—β. By heating ammonium formate by itself to between 160° and 200°, and leaving the distillate over sulphuric acid, till its weight becomes nearly permanent; formamide then remains as a colourless liquid. A solution of ammonium formate in 4 or 5 pts. water also yields a small quantity of formamide when distilled (Lorin, *Compt. rend.* lix. 51).—γ. By heating a mixture of 1 mol. sodium formate and 1 mol. sal-ammoniac, carbon monoxide being then also evolved. If calcium formate be substituted for the sodium salt, a higher temperature is required, less formamide is produced, and the gas evolved contains 2 vol. carbon monoxide to 3 vol. hydrogen, with small quantities of hydrocarbons, hydrocyanic acid, and ammonium carbonate (Lorin, *ibid.* 788).

Formamide mixes with ether containing alcohol, but not with pure ether. With sodium it decomposes, producing explosion and ignition. Heated with zinc-sodium or sodium-amalgam, it emits the odour of methylamine, and yields a residue containing cyanides; with zinc-sodium in the cold, only ammonia is given off, and the residue does not contain cyanides. Strong potash solution eliminates ammonia from it at ordinary temperatures. With alcohol and hydrochloric acid, it yields sal-ammoniac and ethyl-formate.

Methyl-formamide. $C^2H^5NO = (CHO.CH^3.H)N$ (Linnemann, *Wien. Akad. Ber.* lx. 44; *Chem. Centr.* 1870, 138).—This compound, isomeric with acetamide, is produced by evaporating the aqueous solution of methylamine formate to a syrup, distilling, evaporating the aqueous distillate on the water-bath, and redistilling with potassium carbonate, which does not decompose this amide or its homologues. It is a thickish, scentless liquid, of sp. gr. 1·011 at 190°, boiling at 190° (under a pressure of 0·14 met.), burning with a faintly violet-edged flame, soluble in all proportions of water and alcohol, insoluble in ether; resolved by boiling with strong aqueous potash into methylamine and formic acid, and by boiling with dilute sulphuric acid into carbon monoxide and methylamine: $(CHO.CH^3.H)N = CO + CH^3.H^2.N$. This last decomposition is also produced by phosphoric anhydride at ordinary temperatures, hydrocyanic acid being also found amongst the volatile products.

Ethyl-formamide. $(CHO.C^2H^5.H)N$.—Prepared like the preceding. Colourless, thickish, nearly scentless liquid, burning with a bright flame. Sp. gr. 0·952 at 21°. Boils at 196°–197°. Soluble in all proportions of water, alcohol, and ether; easily separated from aqueous solution by potassium carbonate. At −30° it becomes thicker, but does not solidify. By prolonged boiling it is for the most part resolved into carbon monoxide and ethylamine. By strong potash-solution it is resolved slowly in the cold, quickly at the boiling heat, into ethylamine and formic acid; similarly by sodium-amalgam. Phosphoric anhydride acts upon it in the same way as on methyl-formamide. Fused and pulverised zinc chloride decomposes it at incipient boiling heat into carbon monoxide, ethylene, and ammonia (Linnemann, *loc. cit.*).

Diethyl-formamide, $CHO.(C^2H^5)^2.N$, is prepared by heating a mixture of diethylamine and formic acid. Colourless, scentless, thickish liquid, of sp. gr. 0·908 at 19°, not solidifying at −20°, boiling at 175°–178°, easily soluble in alcohol, ether, and water; separated from aqueous solution by potassium carbonate, as a light layer of liquid (Linnemann, *loc. cit.*).

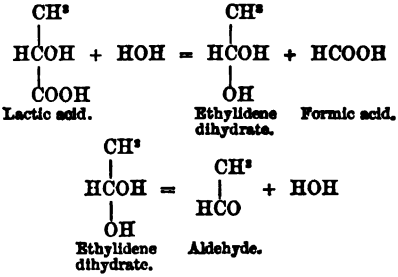
FORMENE. Syn. with METHANE.

FORMIC ACID. $CH^2O^2 = H—COOH$.—Produced, according to Maly (*Jahresb.* 1865, p. 297), by the action of sodium-amalgam on aqueous ammonium carbonate;

also, though in smaller quantity, by boiling finely granulated zinc and zinc carbonate with potash-ley. It is likewise formed by exposing carbon bisulphide to sunshine in sealed tubes containing a little water (Loew, *Zeitschr. f. Chem.* [2] iv. 622):

$$CS^2 + 2H^2O = CH^2O^2 + H^2S + S.$$

Thirdly, it is formed, together with aldehyde, by boiling ordinary lactic acid for several hours with dilute sulphuric acid, the reaction appearing to take place by two stages, and ethylidene dihydrate, $CH^3.CH(OH)^2$, isomeric with glycol, being formed as an intermediate product; thus:



$$\underset{\text{Lactic acid.}}{\begin{matrix} CH^3 \\ | \\ HCOH \\ | \\ COOH \end{matrix}} + HOH = \underset{\text{Ethylidene dihydrate.}}{\begin{matrix} CH^3 \\ | \\ HCOH \\ | \\ OH \end{matrix}} + \underset{\text{Formic acid.}}{HCOOH}$$

$$\underset{\text{Ethylidene dihydrate.}}{\begin{matrix} CH^3 \\ | \\ HCOH \\ | \\ OH \end{matrix}} = \underset{\text{Aldehyde.}}{\begin{matrix} CH^3 \\ | \\ HCO \end{matrix}} + HOH$$

(Erlenmeyer, *Zeitschr. f. Chem.* [2] iv. 343).

Preparation.—Lorin (*Bull. Soc. Chim.* [2] v. 7, 12) obtains aqueous formic acid of 75 p. c. by distilling dehydrated oxalic acid with glycerin; the decomposition begins below 50°, and the temperature must be carefully regulated, on account of the frothing which takes place.

Crystallisable formic acid is more easily obtained from the copper salt than from the lead salt by decomposition with hydrogen sulphide. A better method of preparing it is however to dissolve dehydrated oxalic acid at a gentle heat in aqueous formic acid of 70 p. c., decant the liquid when cold from the crystallised oxalic acid, and distil the portion which remains liquid. The nearly anhydrous distillate when well cooled deposits crystallisable formic acid. Cupric formate heated by itself yields formic acid of 87 p. c. When formic acid of about 57 p. c. is left over concentrated sulphuric acid, there ultimately remains an acid of 63 p. c., corresponding in composition with the hydrate $2CH^2O^2.3H^2O$ (Lorin).

Decompositions.—A mixture of formic acid, CH^2O^2, with an equal volume of water, electrolysed with a battery of moderate power (4 Bunsen's elements), gives off at the positive pole a mixture of carbon dioxide and oxygen; so likewise does a solution of 37 pts. sodium formate in 63 pts. water; potassium formate mixed with potash gives off only carbon dioxide (Burgoin, *Ann. Ch. Phys.* [4] xiv. 157). By chromic acid, formic acid is completely oxidised to water and carbon dioxide (Chapman, *Chem. Soc. J.* [2] v. 289); also by potassium permanganate, either in alkaline or in acid solution (Berthelot, *Jahresb.* 1867, p. 335). With strong aqueous hydriodic acid, it yields water and carbon monoxide. Methyl-formate similarly treated is converted into carbon monoxide, water, and methane (Berthelot, *ibid.* p. 345).

On the antiseptic properties of formic acid, see p. 615.

Metallic Formates. *Iron Formates.*—*Ferrous formate*, $(CHO^2)^2Fe + 4H^2O$, forms green crystals only slightly soluble in cold water, more easily in formic acid, insoluble in alcohol. *Ferric formate*, $(CHO^2)^6Fe^2 + H^2O$, is deposited from a solution of recently precipitated ferric hydrate in formic acid, in yellow shining crystals, easily soluble in hot water; when ignited it leaves ferric oxide still in the form of the crystals. The neutral ferrous salt, when exposed to the air, deposits ferric hydrate, while a more or less basic ferric formate remains dissolved. On boiling the solution of the ferrous salt in an open vessel, a basic ferric salt is deposited, containing $(Fe^2)^{vi}\left\{\begin{matrix} CHO^2 \\ (OH)^5 \end{matrix}\right.$.

Ferric triformonitrate, $Fe^2\left\{\begin{matrix} (CHO^2)^3 \\ NO^3 \\ (HO)^2 \end{matrix}\right. + 3H^2O$, is deposited, on evaporating in a vacuum a solution of ferrous formate oxidised by nitric acid, in red, iridescent, very easily decomposible crystals, while the mother-liquor retains neutral ferric formate. *Ferric dichlorotetraformate*, $Fe^2(CHO^2)^4Cl^2 + 3H^2O$, separates gradually from a solution of ferrous chloride in formic acid oxidised by nitric acid in reddish-yellow nodules slightly soluble in alcohol. *Ferric diformodiacetonitrate*, $Fe^2\left\{\begin{matrix}(CHO^2)^2\\(C^2H^3O^2)^2\\NO^3\\HO\end{matrix}\right.$ + $5H^2O$, is formed by oxidising a mixture of equivalent quantities of ferrous formate and acetate with nitric acid, and separates from the solution, by evaporation over sulphuric acid, as a red, crystalline, very deliquescent mass which gradually loses 3 mol. water (Scheurer-Kastner, *Ann. Ch. Phys.* [3] lxviii. 472).

Lead Formates (Barfoed, *J. pr. Chem.* cviii. 1; *Chem. Centr.* 1870, 171).—**Normal lead formate**, $(CHO^2)^2Pb$, is usually said to dissolve in 36 pts. of cold and 5·5 pts. of boiling water.

Basic salts.—The *biplumbic* salt $(CHO^2)^2Pb.PbO$ or $2PbO.C^2H^2O^3$ is produced by briskly agitating a solution of the normal salt saturated at ordinary temperatures with an equivalent quantity of finely pulverised lead oxide, or by treating a boiling solution of the normal salt, three or four times as strong, with lead oxide, heating the liquid to 100° in a closed flask till it becomes quite clear, and leaving it to cool slowly. It then separates in colourless, transparent, shining, heavy, needle-shaped crystals, somewhat more soluble in cold water, and somewhat less soluble in hot water than the normal salt; distinguished, moreover, from the latter by the property that its solution is strongly alkaline and gives a copious precipitate with carbonic acid. Soluble in 58·7 pts. of cold and 10 pts. of boiling water; insoluble in alcohol; the aqueous solution is completely precipitated in 12 to 24 hours, when mixed with about six times its volume of alcohol. Biplumbic formate is likewise precipitated on mixing a solution of 2 eq. of the normal salt with 1 eq. of alkali. Its aqueous solution added to a warm solution of sodium sulphate in excess forms a crystalline precipitate of biplumbic sulphate, $SO^4Pb.PbO$.

Triplumbic Formate, $(CHO^2)^2Pb.2PbO$ or $3PbO.C^2H^2O^3$, produced by boiling a solution of the normal salt with 2 mol. lead oxide, or by mixing the solution of the normal salt with $\frac{2}{3}$ mol. soda, or with rather more than $\frac{2}{3}$ mol. ammonia, forms colourless, silky, slender, needle-shaped crystals, having a silky lustre, and a beautiful zeolitic aspect while immersed in the liquid, but falling to pieces when it is poured off. Soluble in 25·5 pts. cold and 7·5 pts. boiling water, forming a strongly alkaline solution which gives a copious precipitate with carbonic acid. By prolonged boiling it loses formic acid, as do likewise the solutions of the preceding salts.

Quadriplumbic Formate, $(CHO^2)^2Pb.3PbO$ or $4PbO.C^2H^2O^3$, is produced by boiling a strong solution of the tribasic salt with a large quantity of lead oxide, or by digesting a solution of the same salt saturated at ordinary temperatures with lead oxide at 100° for a week. It is thus obtained as a bulky, dirty yellow precipitate, appearing under the microscope as a mixture of slender needles and unaltered lead oxide. Soluble in about 90 pts. of cold water; insoluble in alcohol (Barfoed).

Alcoholic Formates. *Formic Ethers.*—These ethers are easily prepared in considerable quantity by distilling equivalent quantities of oxalic acid and the corresponding alcohols with dehydrated glycerin. The vapours are allowed for some time to fall back into the retort, the ether not being distilled off till the oxalic acid is completely decomposed: 500 grms. amyl alcohol thus treated yield an equal weight of amyl formate (Lorin, *Bull. Soc. Chim.* [2] v. 7, 12).

Allyl Formate, $C^4H^6O^2 = CHO^2.C^3H^5$, is obtained as a secondary product, in the preparation of formic acid by distilling oxalic acid with glycerin. On rectifying the crude product, this ether passes over first, and floats as an oil on the first portions of the distillate. When purified by washing with water and sodium carbonate, and dried with calcium chloride, it forms a light yellow ethereal liquid having an extremely irritating odour, like allyl compounds in general, boiling at 82°–83°, and having a sp. gr. of 0·9322 at 17·5°. Caustic potash resolves it into allyl alcohol and formic acid. The mode of its formation in the process just mentioned is not yet understood: perhaps a glyceryl formate is produced in the first instance, and afterwards decomposed as the temperature rises (Tollens, *Zeitschr. f. Chem.* [2] ii. 518; Tollens a. Weber, *ibid.* iv. 441).

Ethyl Formate. $C^3H^6O^2 = CHO^2.C^2H^5$.—Löwig a. Weidmann observed that this ether when treated with sodium gives off pure carbon monoxide, without admixture of hydrogen, and likewise yields sodium ethylate, alcohol, and sodium formate. According to Wanklyn (*Zeitschr. f. Chem.* [2] iv. 674), the reaction is in the first instance analogous to that which takes place with ethyl acetate, yielding sodium-triformyl and sodium ethylate:

$$3\left.\begin{matrix}CHO\\C^2H^5\end{matrix}\right\}O + Na^4 = (CHO)^3Na + 3C^2H^5NaO,$$

the sodium triformyl being then resolved into sodium methylate and carbon monoxide:

$$(CHO)^3Na = 2CO + CH^3NaO.$$

The greater part of the carbon monoxide however is due to the decomposition of the excess of ethyl-formate under the influence of the sodium ethylate, the products being carbon monoxide and alcohol: $C^3H^6O^2 = CO + C^2H^6O$. Direct experiments by Geuther (*Zeitschr. f. Chem.* [2] iv. 655) have indeed shown that ethyl formate is decomposed in this manner when heated in sealed tubes with sodium ethylate, the latter remaining unchanged.

Ethyl Orthoformate. $C^7H^{16}O^3 = (CH)'''(OC^2H^5)^3$.—This ether, discovered by Williamson a. Kay (*Proc. Roy. Soc.* vii. 135), is produced by the action of chloroform on sodium ethylate, or by heating chloroform with a solution of potash in absolute alcohol:

$$CHCl^3 + 3C^2H^5NaO = 3NaCl + CH(OC^2H^5)^3.$$

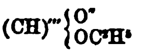
Ladenburg a. Wichelhaus (*Bull. Soc. Chim.* [2] ix. 356) prepare it by dropping a mixture of absolute alcohol and chloroform on sodium (1 mol. chloroform to 3 at. sodium), under a layer of ether. A brisk reaction takes place at first, after which the mixture is distilled, first over a water-bath, then over an oil-bath, and the portion which distils above 110° is washed, dried, and rectified: 170 grms. sodium treated in this manner with about 300 grms. chloroform and 350 grms. absolute alcohol yielded 50 grms. ethyl orthoformate.

Ethyl orthoformate is a colourless, aromatic, easily inflammable liquid having a sp. gr. of 0·8694, remaining liquid at −18°, and boiling at 145°–146° (Kay), at 146°–148° (Ladenburg a. Wichelhaus). Bromine decomposes it at ordinary temperatures, yielding ethyl bromide, ethyl carbonate, ordinary ethyl formate, and alcohol (L. a. W.):

$$2CH(OC^2H^5)^3 + Br^2 = 2C^2H^5Br + CO(OC^2H^5)^2 + CHO(OC^2H^5) + C^2H^6O.$$

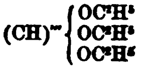
Heated in sealed tubes with aqueous ammonia or ethylamine, it yields crystals of ammonium or ethylammonium formate. With perfectly anhydrous alcoholic ammonia a base is obtained which yields a well-crystallised platinum salt. With aniline it yields methenyl-diphenyl-diamine, $(CH)'''(C^6H^5)^2HN^2$ (Wichelhaus, *Zeitschr. f. Chem.* [2] v. 284).

The relation between orthoformic ether and ordinary formic ether may be represented by the following formulæ:



$$(CH)'''\left\{\begin{matrix}O''\\OC^2H^5\end{matrix}\right.$$

Formic.



$$(CH)'''\left\{\begin{matrix}OC^2H^5\\OC^2H^5\\OC^2H^5\end{matrix}\right.$$

Orthoformic.

FORMIC ALDEHYDE. $CH^2O = H.COH$. *Methylic Aldehyde* (Hofmann, *Proc. Roy. Soc.* xvi. 156).—This compound, which may also be regarded as the ketone of formic acid, is produced when a current of air charged with vapour of methyl alcohol is passed over a glowing spiral of platinum wire. A three-necked bottle having a capacity of 2 litres is filled to about 2 centim. with gently warmed methyl alcohol. Through one of the necks passes a tube reaching to the surface of the liquid; the second is fitted with a cork carrying a spiral of platinum wire, also reaching to the surface of the liquid; and the third is connected with a Liebig's condenser, the lower extremity of which is fitted into a two-necked receiver. The second tubulus of this receiver is connected with a series of wash-bottles, the last of which is connected with an aspirator. The apparatus being thus prepared, the platinum spiral is heated to whiteness and introduced into the three-necked bottle. In a few seconds the slow combustion of the methyl alcohol is made evident by the irritating odour emitted, the whole apparatus at the same time becoming heated, and drops of liquid collecting in the receiver. The apparatus is now in good working order, and if the stream of air be properly regulated, the platinum wire may be kept glowing uninterruptedly for hours, or even days.

The liquid which collects in the receiver is a solution of formic aldehyde in methyl alcohol. When rendered slightly alkaline by ammonia and gently warmed with silver nitrate, it yields a beautiful specular deposit of silver, with greater ease even than common acetic aldehyde. The same solution heated with a few drops of caustic potash, deposits drops of a brownish oil having the odour of the resin of acetic aldehyde.

Formic aldehyde has not yet been obtained in the pure state; but on treating its solution with hydrogen sulphide, and heating the resulting liquid with strong hydrochloric acid, it solidifies on cooling to a dazzling white mass of felted needles, consisting of the corresponding sulphur-compound CH^2S.

According to E. Mulder (*Zeitschr. f. Chem.* [2] iv. 265), formic aldehyde is also produced by the dry distillation of calcium formate. Formic sulphaldehyde is one of the products of the action of nascent hydrogen on sulphocyanic acid: $SCNH + 2H^2 = NH^3 + CH^2S$ (Hofmann, *Zeitschr. f. Chem.* [2] iv. 689).

FORMOBENZOIC ACID. Syn. with MANDELIC ACID (iii. 799).

FRANGULIC ACID and **FRANGULIN.** Frangulin, the yellow colouring matter of the bark of the berry-bearing alder (*Rhamnus Frangula*), has lately been examined by A. Faust (*Zeitschr. f. Chem.* [2] v. 17), who finds that in the pure state, as prepared by Casselmann's process (ii. 706), it has the composition $C^{20}H^{20}O^{10}$, and that it is a glucoside, being resolved by acids into sugar and frangulic acid:

$$C^{20}H^{20}O^{10} + H^2O = C^6H^{12}O^6 + C^{14}H^{10}O^5.$$

Frangulic acid, $C^{14}H^{10}O^5 + H^2O$, may also be prepared directly from the bark by boiling it with water containing soda instead of ammonia, as in the preparation of frangulin. It is an orange-yellow, loosely coherent, crystalline mass, appearing under the microscope to be composed of long prisms. It melts between 246° and 248°, and gives off its water of crystallisation at 120°; dissolves slightly in water, chloroform, and benzol, easily in alcohol and ethers. Alkalis dissolve it, forming solutions of a fine red colour, from which acids precipitate it unaltered. From its slightly ammoniacal solution, it is precipitated by alkaline earths and by many metallic salts. It dissolves in fuming nitric acid, and the solution when diluted and evaporated, leaves a red mass, probably identical with the nitrofrangulic acid which Casselmann obtained, together with oxalic acid, by the action of fuming nitric acid upon frangulin. *Dibromo-frangulic acid*, $C^{14}H^8Br^2O^5$, is precipitated on mixing an alcoholic solution of frangulic acid with excess of bromine. It is a light-red crystalline mass composed of short slender microscopic needles, sparingly soluble in cold alcohol.

Difrangulic acid, $C^{28}H^{18}O^9 = 2C^{14}H^{10}O^5 - H^2O$, is formed in small quantity in the preparation of frangulic acid from the bark of *Rhamnus Frangula* by boiling with water containing soda, and may be separated from the lead precipitates obtained in the course of the preparation. It is very much like frangulic acid, but has a darker colour; crystallises with 2 mol. water, which are given off at 120°; melts at 248°–250°, that is to say nearly at the same temperature as frangulic acid. This coincidence of melting point appears to be due to the circumstance that frangulic acid, at or a little below its melting point, gives off water and is converted into difrangulic acid.

FRANKLINITE. From an analysis by v. Kobell (*Jahresb.* 1866, p. 922), and a new analysis by Rammelsberg (*ibid.* 1867, p. 979), this mineral appears to have the general formula of the spinels, $MO.M^2O^3$. The mean of Rammelsberg's analyses gave 66·05 p. c. Fe^2O^3, 12·23 Mn^2O^3, and 21·88 ZnO, agreeing with the formula $(\frac{2}{5}MnO.\frac{3}{5}ZnO).Fe^2O^3$.

FRAXIN or **PAVIIN.** From a renewed examination of this substance, obtained from horse-chestnut bark, Rochleder (*J. pr. Chem.* xc. 433; *Jahresb.* 1863, p. 588) concludes that it has the composition $2C^{16}H^{18}O^{10}.H^2O$, and that when heated in a stream of carbon dioxide to 150° (more quickly at 200°) it gives off its water, and then contains $C^{16}H^{18}O^{10}$. After crystallisation from hot alcohol, it is pure white, and gives off its water at 110°–113°. Its decomposition into fraxetin and glucose is represented by the equation:

$$\underset{\text{Fraxin.}}{C^{16}H^{18}O^{10}} + H^2O = \underset{\text{Fraxetin.}}{C^{10}H^8O^5} + \underset{\text{Glucose.}}{C^6H^{12}O^6}$$

FRAXINUS. The leaves of the ash-tree (*Fraxinus excelsior*) contain, according to W. Gintl (*Zeitschr. f. Chem.* [2] iv. 731; v. 377), fat, pectin, a resinous body, optically inactive malic acid (partly free, partly as calcium salt), inosite, mannite, dextroglucose, and a gummy substance not yet examined.

FRUIT. A. Dupré (*Chem. Soc. J.* [2] v. 378) has examined the variations in the proportions of acid and sugar which take place in the ripening of grapes. He finds that a considerable increase in the quantity of sugar is not attended with any essential alteration in the amount of acid: whence it seems to follow that the sugar is not formed from the acid, but that the acid determines the formation of sugar from some other constituents of the fruit.

Sestini (*Bull. Soc. Chim.* [2] vii. 236) has determined the quantities of water, sugar (glucose), and acid in various dried fruits. The numbers in the column headed 'Acid' indicate the volume in cub. cent. of a normal alkaline solution (containing 20 grams soda in a litre) which is neutralised by 100 grams of the fruits.

	Water p. c.	Glucose p. c.	Acid c.c.
Ordinary dry figs	34·38	42·00	10·5
Figs *à pièce*	43·36	45·50	5·2
Marseilles figs	32·67	48·35	5·3
Dates (stoned)	39·18	43·40	2·8
Dried currants (Corinth grapes)	34·64	53·97	36·3
Dry grapes (Zibibbo)	37·83	54·08	17·3
Dry pears * (from Farli)	32·86	23·93	15·4
Black Marseilles plums	31·95	23·28	35·9
White Italian plums	33·09	31·95	56·2

Boussingault (*Ann. Ch. Phys.* [4] viii. 210) has examined the products of fermentation of saccharine fruits. Having observed that the quantity of alcohol obtained by distilling fermented cherry or plum juice, is only a fraction of that which corresponds to the sugar contained in the substances subjected to fermentation, he endeavoured to ascertain the cause of this loss by a comparative estimation of the amount of sugar in the fruit, and of the quantities of sugar and alcohol in the products of the fermentation. In the following table (p. 625) the numbers marked *a* in the column headed 'Glucose' denote the sugar which directly reduces cupric oxide; *b* that which is formed by heating with acids. The 'calculated' numbers denote the quantity of alcohol corresponding to the glucose which disappears in fermentation. The quantity of acid is expressed by its equivalent in hydrogen sulphate, SO^4H^2. All weights are given in grams.

Out of 100 pts. glucose and other kinds of sugar contained in the fresh juice there remained undecomposed by the fermentation:

Of Grapes	Apples	Damsons	Mirabelles	Cherries
1·9 to 3·4	2·8 to 16·7	7·7 to 8	5·9 to 18	35·2 to 38·4 pts.

The fermented juice (1 litre) still contained the following quantities of sugar or saccharine substances:

In Wine	Cider	Damson wine	Mirabelle wine	Cherry wine
4 to 8	4 to 8	6 to 7	12 to 19	40 to 46 grams.

Boussingault surmises that the sugar in wine and cider may gradually disappear in consequence of a slow fermentation, although it had not sensibly diminished after the samples had been kept for a year or two.

Grapes contain only glucose; apples only glucose, with sometimes an invertible sugar (cane-sugar?); but the pulp of stone-fruits contains also non-fermentable substances. Cherries contain, besides glucose, a considerable quantity of a crystallisable substance, which reduces potassio-cupric tartrate, and after treatment with acids is not fermented by yeast: hence it is found in the fermented juice. Damsons and mirabelles contain a substance (gum?) which is converted by acids into fermentable glucose (galactose?), and appears also to undergo this change during the fermentation of the juice, as it disappears, partly at least, during that process. Hence it follows that the estimation of glucose by means of potassio-cupric tartrate before fermentation may lead to totally erroneous results regarding the quantity of alcohol that may be expected, unless it has been previously ascertained that the directly reducing substance is really fermentable sugar, and that the substance which reduces after treatment with acids is cane-sugar or an analogous body.

The amount of acid in wine from the grape is greater than that in must, whether the fermentation takes place with or without access of air; in other fruits, the quantity of acid diminishes in fermentation without access of air. The quantity of alcohol of the fermented product is in all cases less—probably in consequence of evaporation—than that which is calculated from the glucose which disappears; a further loss (about 10 p. c. of the alcohol formed) takes place in the distillation of cherry- and damson-brandy. Black cherries and the variety known as *mérises* contain in their sarcocarp the substances required for the formation of prussic acid, and therefore yield must and fermented products containing that acid, even if the kernels have been previously removed. Damsons and mirabelles, on the other hand (unless mixed with bruised kernels), always yield a distillate free from prussic acid. In a litre of cherry-brandy Boussingault found from 0·120 to 0·183 grm. prussic acid.

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* The pears, for better preservation, had been dipped in boiling water before drying: hence the small amount of sugar.

Fermentation-products of Saccharine Fruits.

Material and Product of Fermentation		Glucose	Alcohol: found.	calc.	Acid
Grapes.					
I. Must with Lees .	13·5 lit.	2472·22	—		94·23
Wine . . .	12·06 „	47·50	1118·5	1239·3	101·43
			=90 p. c.		
II. Must without Lees	2 lit.	446·94	—		7·06
Wine . . .	1·933 „	15·31	201·26	220·61	8·36
			=91 p. c.		
Apples.					
III. Must . . .	19037 grm.	1836·28	—		77·48
Wine . . .	17077 „	135·05	781·23	869·50	71·44
			=89·8 p. c.		
IV. Must with 72 c.c. yeast . . .	2·072 lit.	201·16	—		8·14
Wine . . .	1·810 „	5·66	86·30	99·9	0·86
			=86 p. c.		
Cherries.					
V. Cherry-pulp * without stones .	11·5 lit.	3124·09	—		78·55
After fermentation .	10·694 „	1199·12	902·40	983·80	75·29
			=92 p. c.		
VI. Cherries with kernels	8520 grm.	1349·23	—		26·0
After fermentation .	8117 „	475·20	394·14	446·72	36·98
			=88 p. c.		
Mirabelles.†					
VII. Pulp without kernels	2419·8 grm.	(a) 225·79 (b) 193·07 429·03	—		19·21
After fermentation .	2251·5 „	(a) 47·86 (b) 31·00 78·86	137·93	178·97	13·60
			=76 p. c.		
Damsons.†					
VIII. Pulp without kernels	6639·6 grm.	(a) 504·5 (b) 378·1 822·6	—		47·01
After fermentation .	6220·5 „	(a) 42·20 (b) 23·89 66·09	351·85	387·11	36·71
			=91 p. c.		
Damson-juice.					
IX. Before fermentation	854·40 grm.	(a) 61·31 (b) 45·90 107·21	—		6·22
After fermentation .	808·25 „	(a) 4·69 (b) 3·58 8·27	47·64	50·57	3·95
			=94 p. c.		

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* The number for glucose includes the non-fermentable sweet substance (*infra*). V. Small black sweet cherries (*merises*); VI. Ordinary black cherries.

† In the fermentation of mirabelles and damsons, a white pulverulent substance like inulin settled to the bottom; the yeast formed remained enclosed in the fruit-pulp.

FUCHSINE. See Aniline-dyes.

FUCUS. The ash of various species of fucus has been analysed by E. Marchand (*J. Pharm.* [4] ii. 276; *Ann. Ch. Phys.* [4] viii. 320; *Jahresb.* 1865, p. 640; 1866, p. 703).

FULMINOSE. A modification of cellulose supposed by Blondeau to exist in gun-cotton, and produced by the action of acids or of heat on ordinary cellulose (p. 419).

FUMARIC ACID. $C^4H^4O^4$.—This is an unsaturated acid containing 2 at. hydrogen less than succinic acid. Respecting its constitution, and that of the isomeric compound, maleic acid, see Acids, Organic (p. 47).

Fumaric acid treated with water and sodium-amalgam, or with hydriodic acid, takes up 2 atoms of hydrogen and is converted into succinic acid (ii. 743). According to Kekulé, however (*Ann. Ch. Pharm. Suppl.* ii. 108), zinc dissolves in aqueous fumaric acid, with evolution of hydrogen, forming zinc fumarate; but when fumaric acid is gently heated with zinc and excess of potash-solution, the hydrogen, instead of escaping, attaches itself to the fumaric acid, and converts it into succinic acid. According to v. Victor (*Zeitschr. f. Chem.* [2] iv. 454), when zinc and fumaric acid are placed together in cold water, the zinc is rapidly attacked, without evolution of hydrogen, the fumaric acid gradually dissolves, and the liquid deposits four-sided prisms of zinc fumarate, while succinic acid remains in solution:

$$2C^4H^4O^4 + Zn = C^4H^2Zn''O^4 + C^4H^6O^4.$$

FUMARINE. This base, obtained by Peschier and afterwards by Hennon from *Fumaria officinalis*, has been further examined by Preuss (*Zeitschr. f. Chem.* [2] ii. 414; *Bull. Soc. Chim.* [2] vii. 453), who, however, has not determined its composition. It is described as crystallising in irregular, six-sided, monoclinic prisms, soluble in alcohol, chloroform, benzol, carbon bisulphide, and amyl alcohol, sparingly soluble in water, insoluble in ether. The solution has a bitter taste and alkaline reaction. It is not coloured by strong nitric acid. With strong sulphuric acid it forms a dark violet liquid, which turns brown on addition of non-oxidising agents. The easily soluble acetate crystallises in silky tufts of needles; the sparingly soluble hydrochloride and sulphate in prisms; the platinum and gold salts in octohedrons.

FURFUROL, $C^5H^4O^2$, is evolved in considerable quantity in the preparation of munjistin by boiling munjeet with aluminium sulphate (iii. 1061); also in the preparation of garancin by boiling ordinary madder with sulphuric acid (Stenhouse, ii. 751).

Furfurol is the aldehyde of pyromucic acid, $C^5H^4O^3$, and is converted into that acid by oxidation with silver-oxide (ii. 752), or better by boiling with concentrated alcoholic potash (Ulrich, *Jahresb.* 1860, p. 269). According to Limpricht (*Zeitschr. f. Chem.* [2] v. 599), furfuric alcohol is produced at the same time:

$$\underset{\text{Furfurol.}}{2C^5H^4O^2} + KHO = \underset{\text{Pyromucate.}}{C^5H^3KO^3} + \underset{\substack{\text{Furfuric}\\\text{alcohol.}}}{C^5H^6O^2}$$

The furfuric alcohol may be extracted from the product by agitation with ether; and the residue decomposed by sulphuric acid yields pyromucic acid, which may then also be extracted by agitation with ether.

According to Stalman (*Jahresb.* 1867, p. 586), furfuric alcohol may be obtained by the action of sodium-amalgam on furfuric (? pyromucic) acid, in the form of a light brown viscid liquid, insoluble in water and decomposed by distillation.

G

GADOLINITE. This mineral has been regarded by some crystallographers as orthorhombic (Nordenskjöld, *Jahresb.* 1859, p. 779; Scheerer, *ibid.* 1861, p. 988; V. v. Lang, *Phil. Mag.* [4] xxviii. 145), by others as monoclinic. Waage (*Jahresb.* 1867, p. 986) found large well-defined crystals from Hitteröe to be combinations of the monoclinic prism ∞P with the pyramidal face P and several secondary faces, and having the clinodiagonal, othodiagonal, and principal axis in the ratio 0·6249 : 1 : 1·31713. Descloizeaux and Damour showed in 1860 (*Ann. Ch. Phys.* [3] lix. 357) that some varieties of gadolinite are monorefractive, some birefractive, and others mixtures of the two kinds. In a recent paper (*Ann. Ch. Phys.* [4] xviii. 305) Descloizeaux reports: (1) That the crystals of gadolinite from Hitteröe, measured by himself and Waage, and analysed by Scheerer, have an energetic bi-axial refraction on two optic axes; the orientation of these axes, that of their bisectrix, and their *inclined* dispersion, prove that the primitive form is an oblique rhomboïdal prism (? triclinic) whose plane of symmetry is the same as that of the axis: this variety contains from 10 to 12 p. c. of glucina. (2) The most homogeneous of the Ytterby crystals measured by von Lang, and analysed by Berlin, are monorefractive; they exhibit a certain number of peculiar modifications, in addition to those shown in the Hitteröe crystals, of which they are the pseudomorphs, and they do not contain glucina. (3) The heterogeneous specimens are forms in transition from the first to the second variety; they contain from 2 to 6 p. c. of glucina. These three kinds of gadolinite differ entirely in their symbolic chemical relations. The birefractive kind has the formula $3M''O.SiO^2$; the monorefractive is a sort of peridote $2M''O.SiO^2$ or M''^2SiO^4; and the transition-forms give an undecided result, the ratio between the oxygen of the silica and that of the bases varying between 3 : 4 and 4 : 5. These differences of constitution probably originate in local circumstances. The Hitteröe mineral appears to be associated with malacone and polycrase in a granitic vein composed of quartz, orthoclase, and oligoclase (with a little mica), and crossing the gabbro of which the greater part of the island of Hitteröe is formed; but that of Ytterby is chiefly accompanied by yttrotantalite and fergusonite, and is imbedded over a red lamellar orthoclase, divided by large plates of black mica.

On the behaviour of gadolinite when heated, see Church (*Chem. Soc. J.* [2] ii. 416).

GAÏDIC ACID. See HYPOGÆIC ACID.

GALBANUM. This resin fused with potash yields resorcin, $C^6H^6O^2$ (iv. 215).

GALLIC ACID, $C^7H^6O^5$, occurs, according to Phipson (*Chem. News*, xx. 116), together with ellagic and nucitannic acids, in the episperm of walnuts. According to von Tieghem (*Compt. rend.* lxv. 1091), the formation of gallic acid in a solution of tannic acid is especially promoted by the development of the spores of *Penicillium glaucum* and *Aspergillus niger*, the solution being exposed to the air (p. 614). According to Bolley and Bähr (*Zeitschr. f. Chem.* [2] iv. 501), gallic acid is produced from the tannin of the sumach by warming it with sulphuric acid.

A solution of barium gallate treated with excess of silver nitrate yields a black precipitate containing metallic silver, and the filtrate contains an acid which when separated by hydrogen sulphide from its lead salt, exhibits all the properties of quercitannic acid (J. Löwe, *J. pr. Chem.* cii. 111; *Jahresb.* 1867, p. 446; see also Barfoed, *ibid.* p. 447). A certain portion of the gallic acid is at the same time converted into ellagic acid, the greater part of which however undergoes further oxidation; but by using arsenic acid as the oxidising agent, ellagic acid may be obtained in considerable quantity. Its formation from gallic acid is represented by the equation:

$$C^{14}H^{12}O^{10} + O = C^{14}H^6O^8 + 3H^2O$$

(Löwe, *Zeitschr. f. Chem.* [2] iv. 603).

When the solution of acid barium gallate, $(C^7H^5O^5)^2Ba$ (ii. 761), is saturated with baryta-water, a white precipitate is formed which quickly turns blue in contact with the air; but if the precipitation and washing with de-aërated water be performed in an atmosphere of hydrogen, and the precipitate quickly dried in a vacuum over sulphuric acid, it exhibits (at 150°) the composition $C^7H^2\overset{''}{Ba}{}^2O^5$; hence gallic acid appears to be quadribasic. In the air-dried state this barium salt contains 5 mol. or 17 p. c. water (Hlasiwetz, *J. pr. Chem.* ci. 113).

Bromogallic Acid. When gallic acid is triturated with bromine, a brisk action takes place, hydrobromic acid is evolved, and mono- or di-bromogallic acid is formed, according to the proportion of bromine used (Grimaux, *Bull. Soc. Chim.* [2] vii. 479).

Monobromogallic acid, $C^7H^5BrO^5$, crystallises by spontaneous evaporation of the aqueous solution, in small, transparent, yellow, hexagonal plates, becoming white and opaque at 100°; from a hot-saturated solution it crystallises in needles. It is easily soluble in boiling, sparingly in cold water, soluble also in alcohol and in ether; melts above 200° without decomposition; oxidises easily in the air, and is coloured successively rose-red, greenish, and orange-yellow by lime- or baryta-water, orange-yellow by ammonia or potash, black by ferric chloride.

Dibromogallic acid, $C^7H^4Br^2O^5$ (at 135°), is obtained by triturating gallic acid with excess of bromine (2 or 3 pts.) and dissolving the product in three times its weight of boiling water; it is formed also in the preparation of the monobrominated acid and crystallises out after the latter. It forms long brittle needles or prismatic laminæ, which retain 1 mol. water at 100°. Dissolves slightly in cold, more easily in boiling water, in ether and in alcohol, is coloured rose-red, light green, and dark red by lime- or baryta-water, indigo-blue in ethereal solution by baryta-water, and then red by water. Ammonia and potash form with the acid an orange-yellow solution becoming rose-red on dilution; with ferric chloride it forms a black-blue liquid (Grimaux). According to Hlasiwetz (*Bull. Soc. Chim.* ix. 501), dibromogallic acid forms with ferric chloride a splendid violet-blue solution, with ammonia a fiery-red solution afterwards turning brown, and with baryta-water a precipitate which turns blue on agitation.

GAMBOGE (Hlasiwetz a. Barth, *Ann. Ch. Pharm.* cxxxviii. 61; *Jahresb.* 1866, p. 628).—This gum-resin, purified by solution in alcohol, filtration, distillation, and precipitation of the residual liquid with water, froths strongly when fused with potash, giving off vapours smelling like lemon and balm. The fused mass, almost wholly soluble in dilute sulphuric acid, contains (besides much acetic and apparently also butyric acid) four products soluble in ether—viz. phloroglucin; a crystallised acid not precipitated by neutral lead acetate; a crystallisable and an uncrystallisable acid, both of which are precipitated by lead acetate. To separate these products: *a*. The aqueous solution of the residue from the ether-distillation is neutralised with sodium carbonate and then agitated with ether, which dissolves the phloroglucin (6 to 8 grm. from a pound of gamboge).—*β*. The liquid filtered therefrom is warmed, acidulated with sulphuric acid, and then exhausted five or six times with ether. The residue of this ethereal extract is dissolved in water and precipitated by neutral lead acetate. The white bulky precipitate A contains the two precipitable acids; the liquid B filtered therefrom contains the third non-precipitable acid. The lead precipitate A and the liquid B are decomposed with hydrogen sulphide, the lead sulphide is washed with boiling water, and the filtered liquids are evaporated. The filtrate thus obtained from the liquid B still contains, however, a small quantity of the acids precipitable by lead acetate, inasmuch as part of the precipitated lead salt is redissolved by the liberated acetic acid.

The liquid from the lead salt A, evaporated to a syrup and left to itself for several days, yields granular crystals, whilst the other amorphous syrupy acid (not obtained pure) remains in the mother-liquid. The crystallised acid is isomeric with uvitic acid, $C^9H^8O^4$ (v. 971), and is therefore called iso-uvitic acid. After recrystallisation from boiling water with aid of animal charcoal, it forms rather thick, short, prismatic crystals belonging to the rhombic system, often with saddle-shaped faces. It has a strong acid taste and reaction, melts without loss of water at 180°, and solidifies again in the crystalline form. Its *ammonium salt* forms very deliquescent laminæ; the *calcium salt* crystallises from a solution of the ammonium salt mixed with calcium chloride in spherical aggregates; another (probably acid) calcium salt is formed by saturating the acid with calcium carbonate. The *barium salt* $C^9H^6BaO^4$ crystallises in shining scales; the *cadmium salt* $(C^9H^7O^4)^2Cd + 5H^2O$ in warty groups of short prisms; the *silver salt* $C^9H^7AgO^4$ is a bulky precipitate sparingly soluble in cold water, not altered by light.

The acid not precipitable by lead acetate obtained from the liquid B, is pyrotartaric acid, $C^5H^8O^4$.

GASES, ABSORPTION OF. 1. **By Liquids.**—Khanikoff a. Louguinine (*Ann. Ch. Phys.* [4] xi. 412) have shown that the absorption of carbon dioxide by water at a constant temperature is not exactly proportional to the pressure (see p. 404). On the absorption of carbon dioxide by solution of sodium phosphate, see Heidenhain a. Meyer (*Ann. Ch. Pharm. Suppl.* ii. 157; *Jahresb.* 1863, p. 92).

H. Deicke (*Pogg. Ann.* cxix. 156) has determined the absorption-coefficient of hydrogen chloride for water at different temperatures. The results, calculated for a barometric pressure of 760 mm., are given in the following table:

Temperature	Absorption-coefficient	Percentage of HCl in solution	Specific gravity of solution
0°	525·702	45·148	1·2257
4	494·722	44·361	1·2265
8	480·288	43·828	1·2185
12	471·336	43·277	1·2147
14	462·375	42·829	1·2074
18	451·222	42·344	1·2064
18·25	450·660	42·283	1·2055
23	435·034	41·536	1·2013

The experiments of Roscoe (*Chem. Soc. Qu. J.* viii. 14) have shown that the constituents of a gaseous mixture are not always absorbed by water in the proportions required by Dalton's law of partial pressures (ii. 800). This subject has been further examined by W. M. Watts (*Chem. Soc. J.* [2] ii. 88), who finds that the quantity of ammonia absorbed by water from a mixture of ammonia and air, and that of sulphurous oxide absorbed from a mixture of that gas with carbon dioxide, agree with the law of partial pressures. The same chemist has confirmed the fact, previously observed by Roscoe and others, that the quantities of ammonia and sulphurous oxide absorbed by water under different pressures do not vary directly as the pressure.

Berthelot has made the following observations on the absorption of gases by solutions of metallic salts: 1. Ammoniacal cuprous chloride directly absorbs oxygen, carbon monoxide, acetylene, ethylene, allylene, propylene (slightly); it does not act immediately on nitrogen dioxide.—2. A solution of ferrous sulphate in sal-ammoniac and ammonia rapidly absorbs, as is well known, oxygen and nitrogen dioxide, but does not act upon acetylene, allylene, ethylene, propylene, or carbon monoxide.—3. A solution of chromous sulphate in sal-ammoniac and ammonia absorbs oxygen, nitrogen dioxide, acetylene, and allylene, but does not act upon carbon monoxide, ethylene, or propylene.

2. **Absorption of Gases and Vapours by Charcoal.** J. Hunter (*Phil. Mag.* [4] xxv. 364; xxix. 166) finds that different kinds of charcoal absorb gases in different proportions, cocoa-nut charcoal being the most absorbent of all. In the following table the numbers placed opposite the names of the several gases indicate the volumes of gas (reduced to 0° and 760 mm.) absorbed at ordinary temperatures by 1 volume of charcoal ignited and quenched under mercury, the numbers in the first column relating to cocoa-nut charcoal, those in the second to Campeachy-wood charcoal, those in the third to charcoal from vegetable ivory:

Ammonia	171·7	—	130·1	Nitrogen monoxide	70·5	—	—
Cyanogen	107·5	—	—	Hydrogen phosphide	69·1	27·5	—
Nitrogen dioxide	86·3	—	—	Carbon dioxide	67·7	—	—
Methyl chloride	76·4	—	—	Carbon monoxide	21·2	—	—
Methyl oxide	76·2	39·8	64·7	Oxygen	17·9	10·07	—
Ethylene	74·7	—	—				

The experiments with hydrogen phosphide and with oxygen did not give very accordant results; in the case of oxygen the discordance probably arose from formation of carbon dioxide.

Hunter has also determined the absorptive power of cocoa-nut charcoal for a considerable number of vapours (*Chem. Soc. J.* [2] iii. 285; v. 160; vi. 186). The substance to be converted into vapour was enclosed in glass bulbs, which were introduced into a graduated tube filled with warm mercury. This tube stood in a mercury trough, and its upper part was surrounded by a glass vessel, into which the vapour of amyl alcohol (boiling at 127°-131°), or of turpentine oil (at 158°-161°), was introduced for the purpose of heating the vapours. For higher temperatures, the glass vessel was replaced by a copper bath containing paraffin, the upper part of the absorption-tube passing through an aperture in its base. When the liquid in the bulb was completely converted into vapour, the pressure and volume of the vapour were read off; and the charcoal heated to redness out of contact with the air was plunged into the mercury and then introduced into the absorption-tube. At the end of the absorption, which takes place much more quickly than with permanent gases, the temperature and pressure were again determined.

In Table I., V denotes the number of volumes of vapour absorbed by 1 vol. of cocoa-nut charcoal; T the mean of the temperatures at the beginning and end of the experiment; P the pressure at the beginning; and P′ that at the end of the absorption. In Tables II. and III., T denotes the mean of the temperatures at the beginning of the several experiments; T′ that of the temperatures at the end of the absorption; V, P, and P′ have the same significations as before.

A comparison of the numbers found in the case of mixed alcohol and water vapours at different temperatures (Table III.) shows that the absorption is greatly increased when one of the vapours is at a temperature near to its point of condensation. Thus at 100° one volume of cocoa-nut charcoal absorbs 187·2 vol. of a mixture of alcohol and water-vapour in equal volumes, and 255·4 vol. of a mixture of 1 vol. alcohol-vapour and 3 vol. water-vapour; at 160°, on the other hand, the absorption diminishes with the increased proportion of water, from 58·1 to 37·6. At the higher temperature, in fact, both the alcohol and the water are absorbed as vapours, and the alcohol is absorbed in larger proportion than the water: hence the diminished absorption of the mixed vapour with the increase in the proportion of water; but at 100° a portion of the water-vapour absorbed by the charcoal becomes liquefied, and the water thus formed within the pores of the charcoal absorbs a considerable quantity of the alcohol-vapour, this effect of course increasing with the proportion of water-vapour in the mixture. The alcohol-vapour in this case is absorbed partly by the charcoal, partly by the water condensed within its pores. In accordance with this view, it is found that vapour of water mixed with gaseous ammonia (as obtained by heating aqueous ammonia) is much more largely absorbed than either ammonia gas or water-vapour separately (*Chem. Soc. J.* [2] viii. 73).

In a recent paper (*ibid.* ix. 76) Hunter has further examined the effects of pressure on the absorption of gases by charcoal.

TABLE I.—*Absorption of Vapours by Charcoal.*

	V	T	P	P′
			mm.	mm.
Water	43·8	127·5	629·1	623·5
"	23·7	158·8	·692·3	694·3
Carbon bisulphide	91·2	157·8	658·1	658·6
" "	117·2	100·0	671·0	671·2
Methyl alcohol	60·5	158·8	685·0	683·8
" "	126·6	127·7	681·3	662·9
" "	150·7	100·0	663·3	651·6
" "	153·4	90·6	707·6	708·6
Amyl alcohol	27·8	159·1	688·9	690·4
Ethyl alcohol	83·4	158·7	665·2	663·1
" "	110·8	126·5	664·6	644·3
" "	141·1	100·0	653·8	652·3
" "	145·8	89·5	707·2	710·2
Benzene	58·7	129·0	660·6	645·6
Ether	54·3	159·0	686·6	683·6
"	68·3	127·8	664·4	660·8
"	87·0	100·0	648·1	643·4
Chloroform	20·8	158·6	657·5	660·2
"	29·5	100·0	646·7	650·7
Acetic acid	33·1	158·7	684·4	675·9
Ammonia	21·9	126·2	661·0	655·4
Carbon dioxide	16·6	126·5	683·0	686·9

Table II.—*Absorption of Vapours by Cocoa-nut Charcoal.*

	V	T	T′	P	P′
		°	°	mm.	mm.
Aniline	110·7	196·8	199·1	603·3	592·0
Phenol	102·0	195·3	194·0	597·1	585·0
Bitter Almond oil	101·1	196·7	196·5	570·8	561·5
Butyric acid	84·3	197·3	197·5	588·1	570·0
Ethyl butyrate	74·9	197·2	195·8	600·6	594·1
Oil of turpentine	48·0	195·3	193·0	588·3	581·2
Valeric acid	41·2	197·8	197·3	581·5	574·5
Aldehyde	66·6	154·3	155·0	683·9	686·8
”	138·7	100·0	100·0	687·1	680·8
Ethyl acetate	71·5	154·1	153·6	691·7	678·7
” ”	116·0	100·0	100·0	676·4	665·2
Acetone	68·0	156·0	156·8	691·1	671·4
”	104·5	100·0	100·0	654·6	641·9
Ethyl nitrite	63·5	100·0	100·0	660·8	660·6
Ethyl chloride	60·4	100·0	100·0	672·5	668·4
Formic acid	30·7	156·4	158·3	696·7	689·1
Amylene	18·4	155·3	155·5	652·6	652·4
Carbon tetrachloride	3·7	154·5	154·5	698·3	694·5
” ”	3·9	100·0	100·0	682·4	635·8
Ethylamine	56·7	186·3	184·4	611·8	590·8
”	91·7	147·9	146·8	674·2	660·9
”	124·5	100·0	100·0	704·6	688·3
Triethylamine	34·5	182·4	182·7	581·2	574·9
Ethyl iodide	36·2	100·0	100·0	697·7	691·8
Methyl acetate	95·9	100·0	100·0	685·2	661·0
Ethyl oxalate	56·2	194·5	195·5	580·8	576·4
Salicylol	38·3	197·0	197·5	588·7	585·4
Salicylic acid	42·9	230·1	229·9	590·7	570·5
Amyl iodide	12·2	161·4	162·3	678·2	676·5
Naphthalene	80·2	230·2	230·7	595·6	572·3
Camphor	25·3	226·1	226·4	621·6	614·9
Nitrobenzene	45·6	225·3	225·6	585·3	563·0
Carbon bisulphide	81·7	191·7	191·3	590·3	564·4
Acetone	52·4	190·0	190·9	562·0	550·2
Ethyl alcohol	87·0	156·2	157·5	711·2	699·7
” ”	72·0	191·5	191·1	579·1	544·9
Methyl alcohol	47·3	191·5	192·3	615·3	587·7

Table III.—*Absorption of Mixed Vapours by Cocoa-nut Charcoal.*

	V	T	T′	P	P′
10 c.c. Alcohol + 4 c.c. Water	182·2	100·0	100·0	695·3	655·9
10 c.c. Alcohol + 10 c.c. Water	187·2	100·0	100·0	723·2	685·2
” ” ” ”	58·1	158·2	158·9	702·1	691·9
10 c.c. Alcohol + 20 c.c. Water	246·1	100·0	100·0	720·6	675·5
” ” ” ”	47·8	158·5	159·1	704·8	694·9
10 c.c. Alcohol + 30 c.c. Water	255·4	100·0	100·0	700·4	672·4
” ” ” ”	37·6	159·4	160·2	706·9	700·9
10 c.c. Methyl alcohol + 10 c.c. Water	226·1	100·0	100·0	695·0	680·3
” ” ” ”	53·6	159·8	160·4	718·8	709·0
10 c.c. Methyl alcohol + 20 c.c. Water	261·3	100·0	100·0	708·9	688·2
” ” ” ”	48·4	160·2	162·0	719·6	708·7
10 c.c. Alcohol + 10 c.c. Acetone	73·9	159·5	160·8	703·4	683·3
10 c.c. Alcohol + 30 c.c. Acetone	72·4	160·5	162·2	704·8	689·0
10 c.c. CCl^4 + 10 c.c. Alcohol	73·5	160·1	161·4	699·2	687·1
30 c.c. CCl^1 + 10 c.c. Alcohol	43·4	159·8	160·7	714·0	708·0
10 c.c. CS^2 + 20 c.c. Alcohol	88·5	160·3	162·8	697·9	679·0

Reichardt a. Blumtritt (*J. pr. Chem.* xcviii. 418; *Jahresb.* 1866, p. 53) have determined the quantity and composition of the gas absorbed by various dry substances on exposure to the air, and expelled from them by heating. The results show that the quantity of the absorbed gases which can be expelled by heat is very different for different substances, and varies in the same substance according to the degree of moisture. The expelled gases rarely exhibit the proportions existing in atmospheric air (as in the case of gypsum), the nitrogen being in almost all cases greatly in excess, whereas oxygen appears to be but sparingly absorbed by the greater number of bodies. [It is probably in many cases absorbed by the solid body, and enters into combination with some of its constituents: charcoal and vegetable mould, for example, may absorb oxygen from the air and afterwards give it out in the form of carbon dioxide.] Carbon dioxide, on the other hand, appears to be an almost invariable constituent of the absorbed gases, and is taken up in especial abundance by ferric oxide, alumina, and clay. Ammonia was found only in very small quantities; carbon monoxide only in organic detritus and in charcoal. Nitric acid also was but rarely found, and when present appeared to be in the form of salts. The following table exhibits the mean results of numerous experiments:

	Gases		100 vol. of the Gases contained			
	from 100 grm. in c.c.	from 100 vol. in vol.	N	O	CO^2	CO
Charcoal from Pine-wood	164·21	—*	100	0	0	0
" " Populus pyramidalis	466·95	195·4	83·60	0	16·50	0
" " Fraxinus excelsior	437·00	159·0	76·03	14·87	9·10	0
" " Alnus glutinosa	287·07	109·9	88·27	0	5·42	6·31
Animal charcoal	84·43	91·3	54·19	0	45·81	0
" " purified with hydrochloric acid	178·01	102·3	93·66	0	6·34	0
Peat	162·58	—	44·44	4·60	50·96	0
Moist Garden soil	13·70	19·9	64·34	2·85	24·06	8·75
Air-dried Garden soil	38·28	53·6	64·70	2·04	33·26	0
Air-dried Ferric Hydrate	375·54	308·6	26·29	3·85	69·86	0
The same gently ignited	39·88	55·5	64·85	11·59	23·56	0
Alumina, air-dried	69·02	82·0	40·60	0	59·40	—
" dried at 100°	10·83	13·6	83·09	16·91	0	—
Manganese dioxide	10·59	26·9	59·86	10·00	30·14	—
Lead oxide	7·38	24·4	90·17	9·83	0	—
Clay	32·89	—	64·72	20·83	14·45	—
" after prolonged exposure to air	25·58	39·05	70·17	4·71	25·12	—
Air-dried room-dust	40·53	48·07	67·69	0	18·61	13·70
Precipitated Calcium Carbonate	65·09	—	80·81	19·19	0	—
Barium Carbonate	16·77	30·8	86·56	13·44	0	—
Strontium "	54·09	58·5	83·58	13·39	3·03	—
Magnesium "	729·21	124·9	63·92	6·72	29·36	—
Finely pounded Gypsum	17·26	—	80·95	19·05	0	—

3. Absorption and Dialytic Separation of Gases by Colloidal Septa and by Metals.

1. By **Caoutchouc**: The experiments of Mitchell in 1831 showed that different gases are absorbed by caoutchouc, and capable of passing through it with different degrees of facility (ii. 818). These phenomena have recently been investigated with great care by Graham (*Phil. Trans.* 1866, p. 399; *Chem. Soc. J.* [2] v. 235). The permeability of thin membranes of caoutchouc by different gases, passing through it either into a vacuum or into other gases, was measured by means of a diffusiometer consisting of a glass tube 1 metre long and 22 mm. in diameter, open at the lower end and closed at top by a thin plate of gypsum, over which the caoutchouc membrane was fastened with copper wire and cemented to the glass with fused gutta-percha. If such a tube be filled with mercury and inverted, a Torricellian vacuum is formed in the upper part, into which the atmospheric air gradually penetrates, passing through the

* The mark — signifies *undetermined.*

caoutchouc film, and depressing the mercurial column. To compare the penetrating power of different gases, a hood of thick vulcanised caoutchouc, provided with a small entrance- and exit-tube for gas, is placed over the upper end of the diffusiometer, and cemented to it with fused gutta-percha. The gas to be operated on can thus be conveyed from the generating apparatus or from the gas-holder into the hood or upper chamber of the diffusiometer, and the excess of gas may be allowed to escape by the exit-tube. The stucco-plate used as a support to the film of caoutchouc, being very porous, and having no absorbing power for gases, does not add sensibly to the resistance experienced by the gases in passing through the caoutchouc. By means of this apparatus equal volumes of different gases were found to pass through the caoutchouc membrane in the times indicated in the following table:

	CO^2	H	O	CH^4	Air	CO	N
Times . .	1	2·470	5·316	6·326	11·850	12·203	13·585

The volumes which pass through in equal times—that is to say, the velocities—are therefore as follows:

	CO^2	H	O	CH^4	Air	CO	N
Velocities .	13·585	5·500	2·556	2·148	1·149	1·113	1

These numbers do not exhibit the relation of the coefficients of gas-diffusion, and therefore show that dialytic penetration is a process essentially different from diffusion, in which nitrogen, for example, penetrates a septum less quickly than the heavier oxygen. They therefore show also that thin membranes of caoutchouc do not possess the porosity of paper, plates of gypsum, or artificial graphite (ii. 813), earthenware tubes, or even gutta-percha, and that they consequently completely arrest the molecular diffusion of gases. The permeation of caoutchouc and other colloïdal membranes by gases appears to takes place in this way: the gas is first absorbed by the colloïdal substance, passes into the liquid state, as when it is absorbed by water, and in that state penetrates the membrane, and volatilises into the vacuum or the gaseous atmosphere on the other side. A lump of caoutchouc immersed for several days in pure oxygen was actually found to absorb 6·82 p. c. of its volume of that gas. The permeability of caoutchouc by gases increases with rise of temperature. Thus the quantity of atmospheric air which passed in a minute through a square metre of silk cloth coated on one side with caoutchouc, into a vacuum, was 0·56 c.c. at 4°, 2·25 c.c. at 14°, and 6·63 c.c. at 60° (all the volumes being reduced to 20° and 760 mm.). These values appear however to vary to some extent with the time during which the particular temperature is kept up, the change in degree of softness of the caoutchouc with change of temperature requiring hours or even days to complete it. The retentive power of caoutchouc for gases appears also to be modified by its softening by heat. Caoutchouc saturated with a gas, and then made rigid by cold, gives up the gas, but very slowly, when subsequently warmed in contact with the air.

When a very thin caoutchouc balloon filled with hydrogen or carbon dioxide is exposed to the air, it contracts, because the gas which escapes outwards is replaced by a smaller volume of air; and as oxygen passes through the caoutchouc more quickly than nitrogen, the air which has entered the balloon is found after a certain time to be richer in oxygen than atmospheric air. Thus when a balloon filled with hydrogen was exposed to the air for three hours, the gas within it was found to consist of 8·98 oxygen, 12·60 nitrogen, and 78·42 hydrogen, giving a proportion of 41·6 vol. oxygen to 58·4 vol. nitrogen; a balloon filled with carbon dioxide and exposed to the air for four hours was found to contain (after absorption of the residual carbon dioxide) 37·1 vol. O to 62·9 vol. N. Similar results were obtained by dialysis into the vacuum of the diffusiometer. When the balloon is left exposed to the air for a considerable time, the proportion of the oxygen to the nitrogen within it diminishes and ultimately sinks to the normal value.

The process of dialytic separation by caoutchouc may be varied in three points: (1) in the condition of the septum, which may consist of a film of caoutchouc formed from caoutchouc varnish, or of distended sheet caoutchouc; (2) in the nature of the support given to the septum, which may be a backing of cotton cloth or of silk, as well as a plate of stucco, earthenware, or wood; and (3) in the means employed for sustaining a vacuum, or at least a considerable degree of exhaustion, on one side of the dialytic septum, while atmospheric air or any other gaseous mixture to be dialysed has access to the other side. A very convenient exhauster for the purpose is Sprengel's mercury-pump, having its vertical tube turned up at the end for the purpose of transferring the gases from one vessel to another, as in the apparatus for water-analysis figured in vol. v. p. 1030. The air to be dialysed may also be compressed on one side of the septum, and left of the usual tension on the other side.

A large number of experiments made under these several conditions showed that, under given circumstances, the dialytic transfer is accelerated by rise of temperature, and retarded by increased thickness of the membrane.

The quantity of air which passed through a square metre of surface of a caoutchouc balloon 0·114 mm. thick was 16·9 c.c. in a minute; through an equal surface 1 mm. thick, 19·2 c.c. in an hour, or 0·32 mm. per minute; and through an elastic air-cushion (vulcanised caoutchouc between two sheets of cotton), 44·95 c.c. in an hour, or 0·749 c.c. per minute.

The usual proportion of oxygen in air once dialysed by caoutchouc is about 41·6 p. c.: it may be described as air deprived of one-half its usual proportion of nitrogen; but a second and a third dialysis would not increase the amount of oxygen in the same proportion, inasmuch as only half the residual nitrogen would be removed at each operation. The practical problem suggested by the air-dialyser is to attain the means, on a large scale, of reducing to one-half or so the proportion of nitrogen in atmospheric acid. Such air will rekindle a glowing slip of wood, and might be applied to many useful purposes.

On the permeability of caoutchouc for gases, see also Aronstein a. Sirks (*Zeitschr. f. Chem.* [2] ii. 260; *Jahresb.* 1866, p. 52).

2. *Action of Metallic Septa at a Red Heat.*—Deville and Troost in 1863 (*Compt. rend.* lvi. 977; lvii. 894, 965; *Jahresb.* 1863, pp. 23, 26) showed that platinum and iron at a red heat are permeable to hydrogen gas. Graham has confirmed this result and finds that red-hot platinum is very much more permeable to hydrogen than caoutchouc at ordinary temperatures. A square metre of sheet caoutchouc 0·014 mm. thick allowed 127·2 c.c. hydrogen gas to pass through it at 20° in a minute, whereas through an equal surface of platinum tube 1·1 mm. thick at a bright red heat, 489·2 c.c. hydrogen passed in the same time. Oxygen, nitrogen, chlorine, hydrochloric acid, carbon dioxide, carbon monoxide, marsh gas, and ethylene, as well as aqueous vapour, hydrogen sulphide, and ammonia, are not capable of passing through red-hot platinum, the last two perhaps because they are decomposed at that temperature, and only hydrogen passes through the metal. For nitrogen, in presence of hydrogen, platinum appears to be permeable to a slight extent.

This peculiar action of platinum may be explained to a certain extent by its property of absorbing hydrogen at a red heat and retaining it for an indefinite length of time at lower temperatures. To demonstrate this property, designated by Graham as 'occlusion,' the metal to be examined, in the form of wire or fragments, is placed within a porcelain tube glazed inside and out, connected at one end with a Sprengel's vacuum apparatus (as in fig. 823, vol. v. p. 1030), and at the other with a gas-generator or gas-holder. The tube, having been exhausted, is gradually heated to redness, while a copious stream of hydrogen (or other gas) is passed through it, and after prolonged ignition, is left to cool slowly. Finally the unabsorbed gas is expelled by a stream of air; the tube is again exhausted and heated to redness; and the gas thereby expelled from the metal is collected and measured.

Platinum wire (drawn from fused platinum and cleansed by washing with caustic alkali and water) gave off, after an hour's agitation in a vacuum, 0·17 vol. hydrogen to 1 vol. platinum (mean of 4 experiments); platinum-sponge similarly treated yielded 1·48 vol.; old wrought platinum (not originally fused), 3·83 to 5·53 vol. hydrogen; platinum foil at 230° took up 1·45 vol., and between 97° and 100°, in three hours, 0·76 vol. hydrogen. The appearance and lustre of the platinum are not altered by this absorption of hydrogen, but after its expulsion the metal appears white and blistered.

Palladium exhibits a much higher absorbing power for hydrogen. In the form of foil, after recent ignition in a vacuum, it takes up, even at ordinary temperatures, 376 times its volume of hydrogen; at 90° to 97°, 643 vol.; at 245°, 526 vol. The spongy metal obtained by igniting palladious cyanide absorbs 686 times its volume at 200°; foil beaten from the fused metal, only 68 vol.; and an alloy of 5 pts. palladium and 4 pts. silver absorbs 20·5 vol. at a dull red heat. The absorbed hydrogen is given off, partly at ordinary temperatures, quickly at a red heat. In this absorbed and condensed state the hydrogen appears to possess intensified affinities, inasmuch as the palladium which has absorbed it reduces ferric to ferrous salts, ferricyanides to ferrocyanides, and in contact with aqueous chlorine or iodine, forms hydrochloric or hydriodic acid. These properties, viewed in connection with the power which palladium possesses of absorbing perceptible quantities of different liquids, were regarded by Graham as tending to support the assumption that the hydrogen thus absorbed passes into the liquid state. The absorptive power of palladium for hydrogen is related to its permeability by that gas, though the two properties are not exactly proportional one to the other. Palladium foil is not permeable at ordinary temperatures to hydrogen, though it is so to ether-vapour. A wrought palladium tube having its sides 1 mm. thick began to give passage to hydrogen through its substance at 240°; at 265°, the quantity of hydrogen which passed in a minute through a square metre of its surface amounted to 327 c.c., and at a heat near redness 423 c.c. When the tube was surrounded with an atmosphere of coal-gas, nothing but pure hydrogen penetrated the palladium, the other constituents of the gaseous mixture remaining without.

Granules of osmiridium do not absorb hydrogen. Copper at a red heat, in the form of sponge absorbs 0·6 vol., in the form of wire 0·306 vol. (wrought copper ignited in a vacuum gives off, together with the hydrogen, small quantities of carbon monoxide). Gold in the form of assay-cornets, which had been recently ignited, took up 0·48 vol. hydrogen, 0·29 vol. carbon monoxide, 0·16 vol. carbon dioxide, when heated in these gases; heated in atmospheric air, it took up from 0·19 to 0·24 vol. of a gaseous mixture in which nitrogen was the prevailing constituent. Pure silver in the form of wire (which when heated alone gave off 0·29 vol. of nearly pure carbon dioxide) absorbed at a red heat 0·211 vol. hydrogen, 0·745 oxygen, and in atmospheric air 0·545 vol. oxygen. Fritted silver obtained by reduction of the oxide exhibited a greater absorbing power, taking up from 6·15 to 7·47 vol. oxygen, 0·907 to 0·938 vol. hydrogen, 0·486 to 0·545 vol. carbon dioxide, and 0·15 vol. carbon monoxide, when heated to redness in these gases. Pure thin silver-leaf ignited in air absorbed 1·37 vol. oxygen, 0·20 vol. nitrogen, and 0·04 vol. carbon dioxide. This oxygenated silver still exhibits the colour and lustre of the pure metal, and retains the oxygen firmly at all temperatures below redness. Thin iron wire, carefully purified with potash-ley and water, yielded, when heated in a vacuum for two hours, 7·94 times its volume, and after seven hours, 12·5 times its volume of a gaseous mixture chiefly consisting of carbon monoxide. Such iron previously heated to redness in a vacuum absorbed at a dull red heat 0·46 vol. hydrogen and 4·15 vol. carbon monoxide. Iron saturated with carbon monoxide remains soft and appears to be incapable of hardening by sudden cooling from red heat; in other respects it does not differ from ordinary iron. The meteoric iron of Lenarto, containing 90·88 p. c. iron, 8·45 nickel, and 0·66 cobalt, yields, when heated in the vacuum apparatus, 2·85 times its volume of a gas consisting almost wholly of hydrogen, with small quantities of carbon monoxide and nitrogen. This fact, viewed in connection with the result established by direct experiment, that wrought iron under the ordinary atmospheric pressure does not absorb more than its own volume of hydrogen, seems to show that the hydrogen contained in the Lenarto iron has been absorbed from a stellar atmosphere denser than that of the earth (*Proc. Roy. Soc.* xv. 502).

3. *Action of Metals at Ordinary Temperatures.*—Palladium, platinum, and iron are also capable of absorbing and retaining at ordinary temperatures considerable quantities of hydrogen, when that element is presented to them in the nascent state. Zinc immersed in dilute sulphuric acid does not take up hydrogen; but thin palladium plate placed in the acid liquid in metallic contact with the zinc becomes charged with hydrogen, which afterwards shows itself on the surface. At the temperature of 12° a palladium plate thus treated took up in an hour 173 times its volume of hydrogen. When employed as the negative electrode of a battery of six Bunsen's elements, it exhibited a still stronger absorption, the evolution of hydrogen being completely suppressed for the first twenty seconds, and the gas absorbed ultimately amounting to 200·4 times the volume of the metal, whereas the same plate on cooling in an atmosphere of hydrogen took up only 90 times its volume. Hydrogen thus absorbed by palladium exhibits no perceptible tension at comparatively low temperatures, and is given off only in traces at ordinary temperatures even in a vacuum, but easily and completely at 100° or when the metal is made to serve as the positive electrode of a decomposing cell; in this case the palladium does not take up any oxygen. Palladium thus charged with hydrogen sometimes becomes suddenly heated on exposure to the air, and then loses its hydrogen by oxidation. *Platinum* under similar circumstances (as negative electrode) likewise takes up hydrogen (2·19 times its volume in one experiment), and is thereby brought into the well-known polarised state; it gives up the combined hydrogen when heated nearly to redness in a vacuum, or when used as positive electrode in a decomposing cell; in this latter case, like palladium, it does not absorb oxygen. Soft *iron* immersed in dilute acid takes up a small quantity of hydrogen (0·57 vol. in one experiment), and gives it up in a vacuum at a red heat.

From these results it appears that at comparatively low temperatures, platinum, palladium, and iron are not permeated by hydrogen, though at higher temperatures hydrogen passes through them with facility. Graham supposed, however, that even in this latter case, a condensation or occlusion of the hydrogen by the metal takes

the suspending wires T, multiplied by the angle of deflection of the coil. Hence the position of equilibrium of the coil, when the current is passing, is determined by the equation

$$\mathrm{CH.A}\sin\beta = \mathrm{T}\,(90^\circ-\beta)$$

or

$$\mathrm{CH} = \frac{\mathrm{T}\,(90^\circ-\beta)}{\mathrm{A.}\sin\beta}\;.\;.\;.\;.\;.\;(a).$$

And the simultaneous observation with the tangent-galvanometer gives

$$\frac{\mathrm{C}}{\mathrm{H}} = \frac{r}{2\pi}\tan\alpha\;.\;.\;.\;.\;.\;(b).$$

The combination of these two equations, (*a*) and (*b*), gives both C and H in absolute measure. (For further details, see F. Kohlrausch, *Pogg. Ann.* [1869] cxxxviii. 1.)

Absolute Measurement of Electromotive Force.—The electromotive force of a galvanic battery, or other equivalent apparatus, may be defined as the quality in virtue of which it tends to do work by the transference of electricity from one point to another; and it may be expressed numerically by the amount of work done during the transfer of the unit quantity of electricity. Thus if W be the work done by the chemical or other forces of the battery, during the transfer of the quantity of electricity Q through the circuit, the electromotive force of the battery may be represented by

$$\mathrm{E} = \frac{\mathrm{W}}{\mathrm{Q}} = \frac{\mathrm{W}}{\mathrm{C}t},$$

the last expression being applicable when the electricity is transferred in the form of a current of uniform strength C lasting for the time *t*. Hence the electromotive force of a battery may also be said to be the work done when a current of unit strength is maintained for unit of time. The work may of course be of various kinds, as, for example, production of heat; work against gravity, as when weights are raised by an electromagnetic engine; work of acceleration against inertia; chemical work, as in a voltameter; magnetic and electrical work, as in an induction coil; but in the above formula it is supposed to be always expressed in absolute mechanical units.

But, just as electromotive force does work in a conducting circuit through the agency of the current which it produces, so, conversely, work done upon a conductor may give rise to electromotive force, and therefore to a current, if the conductor forms part of a closed circuit. This fact, coupled with the condition that the electromotive force developed when unit of work is expended per unit of time is to be taken as the unit of electromotive force, serves as the basis for the absolute measurement of electromotive force. The principles of the measurement will be easily understood from the following considerations.

If a current of the strength C′ circulate in a rectilinear conductor of length l placed at right angles to the lines of force in a uniform magnetic field of intensity H, every element dl of the current is subject to a force equal to

$$\mathrm{HC}'dl$$

in a direction perpendicular to the current and to the lines of force. The resultant force acting upon the whole length l is therefore the sum of the forces acting upon the several elements of it, or

$$\mathrm{F} = \mathrm{HC}'l;$$

and if the conductor be displaced through the distance D perpendicularly to itself and to the lines of force, and in opposition to the force F, a quantity of work w will have been expended in producing the displacement which is expressed by

$$w = \mathrm{FD} = \mathrm{HC}'l\mathrm{D},$$

or, if the displacement take place with the constant velocity v and occupy unit of time, we may write

$$w = \mathrm{HC}'lv.$$

If E be the electromotive force acting in the conductor when at rest, the work (in thi case simply evolution of heat) done in unit of time by the electrical forces when the strength of the current is C′, will be

$$\mathrm{W} = \mathrm{EC}'.$$

But the principle of the Conservation of Energy requires that, when an amount of work w is done upon the conductor by external forces, the equivalent of this work shal the portion soluble in alcohol (mucin or mucedin, ii. 873), for 20 to 24 hours with 2½ pts. sulphuric acid and 6 to 7 pts. water, supersaturating with milk of lime, removing the lime with oxalic acid, the excess of the latter by boiling with lead carbonate, and lastly the dissolved lead with hydrogen sulphide. The strongly acid liquid yields by evaporation a crystalline mixture of tyrosine, leucine, and glutamic acid, from which, by treatment with hot water (which leaves the tyrosine undissolved), and then with alcohol of 30 p. c. (which chiefly dissolves the leucine), and recrystallisation from water (with addition of animal charcoal), and from alcohol of 30 p. c., the glutamic acid is obtained pure. The portion of gluten insoluble in alcohol yields only about 1½ p. c. glutamic acid, but mucedin yields more than 30 p. c., with no tyrosine, and only a small quantity of leucine.

Glutamic acid is likewise obtained, together with aspartic acid and a non-crystallisable body, by treating conglutin with sulphuric acid. On repeatedly boiling the resulting knobby crystalline masses with alcohol of 50–60 p. c., the greater part of the aspartic acid remains undissolved, and an additional quantity of that acid separates from the hot alcoholic solution, while the glutamic acid remains in the mother-liquors, and may be obtained by distillation and concentration over sulphuric acid, in shining tetrahedral crystals.

Glutamic acid dissolves at 15° in 100 pts. water, 302 pts. alcohol of 30 p. c., and 1,500 pts. alcohol of 80 p. c.; at higher temperatures its solubility in water and in dilute alcohol is much greater. The solutions have a strong acid reaction, an astringent taste, and decompose carbonates, forming soluble salts. From hot-saturated solutions the acid separates in white crystalline crusts composed of shining laminæ, by slow evaporation in crystals having a bright adamantine lustre and the form of distorted rhombic octohedrons with basal end-face. Axes $a : b : c = 0{\cdot}8059 : 1 : 0{\cdot}8521$. They are anhydrous, melt with partial decomposition at 135°–140°, then solidify very slowly to a crystalline mass, which decomposes at a higher temperature, emitting an odour like that of burnt horn. It is dextrograte; but when heated with nitrous acid it yields an optically inactive acid homologous with malic acid. The glutamates of the alkali-metals are very soluble, and crystallise with difficulty; those of the alkaline-earth-metals are also very soluble in water and alcohol, and dry up to gummy masses. The *copper salt* separates from aqueous solution in well-defined deep blue crystals, consisting—according to Ritthausen's latest observations—of $C^5H^7NO^4Cu + 2\frac{1}{2}H^2O$; from a very strong solution slightly acidulated with nitric acid, it crystallises in small prisms containing only $2H^2O$, and when precipitated by alcohol, it has the composition $C^5H^7NO^4Cu + 3H^2O$. Lead salts do not precipitate glutamic acid even on addition of ammonia.

GLUTARIC ACID. $C^5H^8O^5$.—An acid homologous with malic acid, produced by the action of nitrous acid on glutamic acid dissolved in dilute nitric acid. It is bibasic. The *calcium salt* $C^5H^6CaO^5 + \frac{1}{2}H^2O$, obtained by neutralisation and precipitation with alcohol, is white, non-crystalline, and flocculent. Decomposed with lead acetate it yields the lead salt in form of a white precipitate, which crystallises from solution in hot water in nodular crystals containing $C^5H^6PbO^5 + \frac{1}{2}H^2O$. In presence of ammonia a basic salt is precipitated. The silver salt is a curdy precipitate, having when dried the composition $C^5H^6Ag^2O^5 + \frac{1}{2}H^2O$. The acid itself crystallises with difficulty from its solution evaporated to a syrup (Ritthausen, *J. pr. Chem.* ciii. 239; *Zeitschr. f. Chem.* [2] iv. 529).

GLUTEN. For a continuation of Ritthausen's investigation of the constituents of gluten (ii. 873), see *J. pr. Chem.* xcix. 462; *Jahresb.* 1864, p. 719.

GLYCERALS. Compounds analogous to the acetals produced by heating glycerin with aldehydes to 170°–200° for 24 to 30 hours:

$$C^3H^8O^3 + \text{Aldehyde} - H^2O = \text{Glyceral}.$$

The following have been obtained:

		B.P.	Sp. gr. at 0°	Vap. density obs.
Acetoglyceral,	$\left.\begin{matrix}C^3H^5\\H\\C^2H^4\end{matrix}\right\}O^3$,	184°–188°	1·081	4·162
Valeroglyceral,	$\left.\begin{matrix}C^3H^5\\H\\C^5H^{10}\end{matrix}\right\}O^3$,	224°–228°	1·027	5·526
Benzoglyceral,	$\left.\begin{matrix}C^3H^5\\H\\C^7H^6\end{matrix}\right\}O$.			

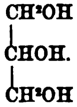
Benzoglyceral can only be partially distilled under ordinary pressure; at 20 mm. pressure it boils between 190° and 200°. It is heavier than water. All the glycerals are insoluble or very slightly soluble in water, inodorous when recently prepared, but are gradually decomposed by moist air, with separation of the corresponding aldehydes (Harnitz-Harnitzky a. Menschutkin, *Bull. Soc. Chim.* [2] iii. 253).

GLYCERIC ACID, $C^3H^6O^4$, is converted by dry distillation, first into pyroracemic acid: $C^3H^6O^4 - H^2O = C^3H^4O^3$; then, with evolution of carbon dioxide, into pyrotartaric acid: $2C^3H^4O^3 - CO^2 = C^5H^8O^4$ (Moldenhauer, *Ann. Ch. Pharm.* cxxxi. 223).

Concentrated glyceric acid heated for several hours to 100° with saturated hydriodic acid is converted into iodopropionic acid (Moldenhauer):

$$C^3H^6O^4 + 3HI = C^3H^5IO^2 + 2H^2O + I^2.$$

Treated with 3 mol. phosphorus pentachloride, it yields chloropropionic acid (Wichelhaus, *Ann. Ch. Pharm.* cxxxv. v. 248).

GLYCERIN. $C^3H^8O^3 = \left.\begin{matrix}(C^3H^5)'''\\H^3\end{matrix}\right\}O^3 =$  $\begin{array}{l}CH^2OH\\|\\CHOH.\\|\\CH^2OH\end{array}$ E. J. Mulder (*Jahresb.* 1863, p. 501) has determined the melting points of frozen aqueous solutions of glycerin of various degrees of concentration:

Glycerin solution .	10°B.	12°B.	14°B.	15°B.
Melting point . .	−9°	−13°	−18°	−21°

The freezing point is very close to the melting point, perhaps a little lower. On mixing snow or finely pounded ice with glycerin, a reduction of temperature equal to 10° or more is produced.

A considerable quantity of glycerin having been sent from Germany to England during a very cold winter (January 1867), was found to be solidified to a crystalline mass resembling sugar-candy, and composed of shining, apparently octohedral crystals of about the size of peas, having a strong refracting power, grating between the teeth, and exhibiting the reactions of chemically pure glycerin. In small quantities they melted quickly, the mass during fusion exhibiting a constant temperature of 7·2°. After complete fusion, the glycerin did not resolidify even when cooled to −18° and agitated (Gladstone, *Chem. Soc. J.* [2] v. 384; Crookes, *Chem. News*, xv. 26). According to Werner (*Zeitschr. f. Chem.* [2] iv. 413), commercial glycerin may be made to crystallise by passing a few bubbles of chlorine into it.

Berthelot found that glycerin fermented in contact with chalk and animal substances yields alcohol (ii. 888). According to Béchamp, the process is more complex, yielding ethyl alcohol and some of its higher homologues, together with acetic, propionic, butyric, and valeric acids; the evolved gases consisted of carbon dioxide, water, and nitrogen (*Zeitschr. f. Chem.* [2] v. 663).

Glycerin oxidised by nitric acid of sp. gr. 1·5 yields—in addition to glyceric acid (ii. 875)—racemic, formic, glycollic, and glyoxylic acids (Heintz, *Ann. Ch. Pharm.* clii. 325).

Glycerin treated with sulphur chloride, as for the preparation of dichlorhydrin (ii. 890), yields also a viscid liquid, which contains chlorine and sulphur, is insoluble in water, sparingly soluble in alcohol, easily in ether, and decomposes, especially in contact with water or moist air, with continued evolution of sulphurous acid and separation of sulphur. It is decomposed by sodium ethylate, yielding ethyl chloride, ethyl oxide, glycerin-mercaptan, and sodium sulphite. It appears to be a mixture or compound of equal molecules of the bodies $O^2Cl.SO.C^3H^5$ and $OSCl.(C^3H^5)H^2$, or it perhaps has the constitution of a chlorinated hyposulphurous ether, $O^2Cl^2.(S^2O)(C^3H^5)^2$ (Wolff, *Ann. Ch. Pharm.* cl. 59).

Glycerides containing Monatomic Alcohol-radicles.—The ethers of this class containing 3 at. ethyl, &c., are formed, similarly to the acetals, by heating acrolein with the corresponding alcohol and a little acetic acid (Alsberg, *Ann. Ch. Pharm.* cxxxi. 123). *Trimethylin*, $C^6H^{14}O^3 = C^3H^5(CH^3)^3O^3$, obtained by heating 1 vol. acrolein, 3 vol. methyl alcohol, and 0·5 vol. acetic acid to 100° for several hours, is a fragrant ethereal liquid, moderately soluble in water, boiling at 148°, and having a sp. gr. of 0·9483 at 0°. *Triethylin*, $C^9H^{20}O^3 = C^3H^5(C^2H^5)^3O^3$, which Reboul a. Lourenço obtained by treating diethyl-chlorhydrin with sodium-ethylate (i. 884), is also produced by heating 1 vol. acrolein, 1 vol. alcohol, and 0·5 vol. acetic acid. It is a fragrant ethereal liquid, moderately soluble in water, boiling at 186°, and having a sp. gr. of 0·8955 at 15°. *Triamylin*, $C^{18}H^{38}O^3 = C^3H^5(C^5H^{11})^3O^3$, appears to be formed by heating 1 vol. acrolein, 3 vol. amyl alcohol, and 0·5 vol. acetic acid to 110°, but is decomposed by distillation.

Diethyl chlorhydrin, $C^3H^4(OC^2H^5)^2(OH)Cl$, is formed by passing hydrochloric acid gas into a mixture of acrolein with 2 vol. absolute alcohol:

$$C^3H^4O + 2C^2H^5(OH) + HCl = C^3H^5(OC^2H^5)^2Cl + H^2O.$$

It is a heavy oily liquid, having a sweetish ethereal odour, and sp. gr. 1·03 at 10·5°. By sodium ethylate in alcoholic solution it is converted into triethylin (Alsberg, *Jenaische Zeitschr.* i. 407).

Nitroglycerin. $C^3H^5(NO^2)^3O^3$.—This compound, related to glycerin in the same manner as gun-cotton to cellulose, is violently explosive, but nevertheless requires the fulfilment of special conditions for the development of its explosive force. Its explosion by the simple application of heat can only be accomplished if the source of heat be applied for a long time in such a manner that chemical decomposition is established in some part of the mass, and is favoured by the continued application of heat to that part. Under these circumstances, the chemical change proceeds with rapidly accelerating violence, and eventually the heated portion is suddenly transformed into gaseous products, which transformation is instantly communicated throughout the whole mass. This result can be obtained more expeditiously and with greater certainty by exposing the substance to the concussive action of a detonation produced by the ignition of a small quantity of fulminating powder, closely confined and placed in contact with or in proximity to the nitroglycerin (Abel, *Chem. Soc. J.* [2] viii. 46). See Combustion, p. 487.

Nitroglycerin is well adapted for blasting, its destructive action being estimated at about ten times that of an equal weight of gunpowder. The first attempts to apply it as a mining agent were made by A. Nobel, a Swedish engineer, in 1864. Some experiments were first made with gunpowder saturated with nitroglycerin. This powder burnt much as usual in the open air, but when confined in shells or blast-holes, it produced greater destructive effects than ordinary powder. Nitroglycerin cannot be employed as a blasting agent in the ordinary way, as the application of flame from a common fuze would not cause it to explode; but when it is introduced in a suitable case into a blast-hole, and a fuze having a small charge of gunpowder attached to its extremity is fixed immediately above it, the concussion produced by the exploding gunpowder effects the explosion of the nitroglycerin. The use of nitroglycerin is, however, attended with very great danger, on account of its great liability to explode by concussion or by friction during transport. Moreover, it solidifies at a temperature probably as high as 8° C. (56° F.), and the friction of the frozen particles is very apt to give rise to explosion. Nobel has, however, found that the danger of accidental explosion of nitroglycerin may be obviated by mixing it with wood-spirit, which renders it non-explosive by percussion or by heat. When required for use, it may be recovered by adding water to the mixture, which precipitates the nitroglycerin. (See Richardson and Watts's *Chemical Technology*, pt. v. p. 395.)

GLYCEROGEL and **GLYCEROSOL.** Graham's names for the gelatinous and soluble compounds of glycerin and silicic acid (v. 1089).

GLYCOCINE. See Glycollamic Acids.

GLYCODRUPOSE. See Drupose (p. 547).

GLYCOGEN. This substance exists in mollusca, especially in oysters, which yield 9·5 p. c. of it (reckoned on the dry weight). *Cardium edule* contains 14 p. c. The glycogen of mollusks is very quickly converted into lactic acid, which, when formed in considerable quantity, protects the animal from putrefaction (G. Bizio, *Compt. rend.* lxii. 675; lxv. 175; *Jahresb.* 1866, p. 752; 1867, p. 741).

From the observations of Tichanowitsch (*On the Origin of Carbohydrates within and without the Organism*, Cracow, 1866, Russian), it appears that glycogen may be produced in four modifications, according to the diet of the animal which yields it—viz. A, produced by exclusively amylaceous diet; B, by feeding with purified white of egg; C, with purified cheese and a little hogs' lard; D, with purified cheese alone. These four modifications differ in solubility and in their action on polarised light:

	$[\alpha]_j$	100 c.c. water dissolve at 100°:
A	+ 199·3	2·5 grams.
B	+ 140	203·9 „
C	+ 170·7	0·328 „
D	+ 211	2·7 „

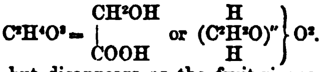
Stscherbakoff (*Zeitschr f. Chem.* [2] vi. 240) has shown that glycogen (prepared from the livers of dogs fed for several days on brown bread after three days fasting) is resolved by boiling with dilute sulphuric acid into glucose and a body, α (together with smaller quantities of other bodies, β, γ, and δ, to be presently noticed), which is precipitated by alcohol as a white amorphous viscid mass, drying up in thin layers to a membrane resembling collodion: it dissolves completely in water to a tasteless liquid; dissolves cupric oxide in presence of alkalis, without reducing it; and is coloured red by iodine. This body α is resolved by boiling with sulphuric acid for six hours into glucose and another body, β, which resembles α in appearance and solubility, is coloured dark red by iodine, and reduces cupric oxide in alkaline solution. β is resolved by boiling with sulphuric acid for three hours into glucose and a third body, γ, which also resembles α in appearance, but is not reddened by iodine, and dissolves cupric oxide in presence of potash without reducing it. This body γ is resolved by boiling with sulphuric acid for two hours into glucose, and a fourth body, δ, similar in external character to α, β, and γ, not coloured by iodine, but capable of reducing cupric oxide in alkaline solution. α, β, and γ are insoluble in strong alcohol; δ dissolves easily in water, sparingly in alcohol. The four bodies α, β, γ, δ are all dextrogyrate, but differ in the amount of their specific rotatory power. Lastly, δ boiled with dilute sulphuric acid is completely converted into glucose without the formation of any other body. From these results, Stscherbakoff infers that δ contains at least 6 atoms of carbon, γ at least 12, β at least 18, α at least 24, and glycogen itself at least 30 carbon-atoms, its formula being $C^{30}H^{50}O^{25}$.

GLYCOLIGNOSE. $C^{30}H^{46}O^{21}$ (J. Erdmann, *Ann. Ch. Pharm. Suppl.* v. 223; *Jahresb.* 1867, p. 738).—A substance remaining after exhausting the wood of the spruce fir (*Abies excelsa*, De C.; *Pinus Abies*, L.) with dilute acetic acid, alcohol, and ether. It is yellowish-white and insoluble in all liquids, yielding only traces of cellulose to ammoniacal copper solution; this behaviour is regarded by Erdmann as showing that in fir-wood, as in the stony concretions of pears (p. 547), the primitive cellulose is associated with another substance. Fir-wood is decomposed by boiling with hydrochloric acid, yielding, together with glucose, from 60 to 65 p. c. of an insoluble body, designated by Erdmann as *lignose*:

$$\underset{\text{Glycolignose.}}{C^{30}H^{46}O^{21}} + 2H^2O = \underset{\text{Glucose.}}{2C^6H^{12}O^6} + \underset{\text{Lignose.}}{C^{18}H^{26}O^{11}}$$

Lignose is reddish-yellow, insoluble in ordinary solvents, and likewise yields to ammoniacal copper solution only small quantities of cellulose. Boiled with dilute nitric acid it leaves a residue of cellulose. Glycolignose fused with potash yields, together with acetic and succinic acids, a substance which appears to be nearly related to pyrocatechin and protocatechuic acid. The same products are obtained with liguose or with glycodrupose, but not with pure cellulose prepared as above. Cellulose may be regarded as pure when the residue left after repeated treatment with nitric acid, dilute ammonia, and water, is no longer coloured by further boiling with nitric acid.

GLYCOLINIC ACID. $C^2H^4O^4$.—A monobasic acid, isomeric with glyoxylic acid, formed, according to Friedländer (*J. pr. Chem.* xciii. 65; *Jahresb.* 1864, p. 366), by the action of sodium-amalgam on ethyl oxalate mixed with 3 pts. of absolute alcohol [pure ethyl oxalate treated with sodium-amalgam yields desoxalic or racemo-carbonic acid, v. 40]. Sodium-glycolinate, the immediate product of the reaction, crystallises in stellate groups of needles or prisms containing $C^2H^3O^4Na + H^2O$, which are easily soluble in water, nearly insoluble in absolute alcohol, and give off their water at 100°. The acid may be separated from a solution of the sodium salt in weak spirit by an alcoholic solution of oxalic acid, and purified by recrystallisation from alcohol. By evaporation over sulphuric acid, it is obtained as a deliquescent radio-crystalline mass, containing $2C^2H^4O^4 + 9H^2O$, and giving off its water of crystallisation at 100°. It is non-volatile, easily soluble in water and in alcohol, has a strongly acid taste, and is decomposed by heating with strong sulphuric acid.

GLYCOLLIC ACID. 

$$C^2H^4O^3 = \begin{array}{l} CH^2OH \\ | \\ COOH \end{array} \text{ or } \left.\begin{array}{c} H \\ (C^2H^2O)'' \\ H \end{array}\right\} O^2$$

—This acid exists in the juice of unripe grapes, but disappears as the fruit ripens (Erlenmeyer, *Jahresb.* 1864, p. 359; 1866, p. 372). It is formed by the action of hydriodic acid, not in excess, upon diglycollic acid (p. 641), and is found among the products of the action of nitric acid upon glycerin (p. 637). Heated with saturated hydrobromic acid to 100° for two days, it is converted into bromacetic acid: $C^2H^4O^3 + HBr = H^2O + C^2H^3BrO^2$ (Kekulé, *Ann. Ch. Pharm.* cxxx. 360). According to Krupsky

(*Zeitschr. Ch. Pharm.* [2] v. 177), glycollic acid yields by dry distillation chiefly dioxymethylene, $C^2H^4O^2$. The formation of this body in small quantity, together with glycollide, in the distillation of glycollic acid, had previously been observed by Heintz (ii. 919), who has since also obtained it, together with glycollic acid, by heating the glycollates of copper and aluminium (*Ann. Ch. Pharm.* cxl. 257):

$$2(C^2H^3O^3)^2Cu = C^2H^4O^2 + 2C^2H^4O^3 + CO + CO^2 + Cu^2O.$$

Calcium glycollate and diglycollate heated with strong sulphuric acid also yield dioxymethylene, together with other products (Heintz);

$$\underset{\text{Glycollate.}}{(C^2H^3O^3)^2Ca} + 3H^2SO^4 = C^2H^4O^2 + SO^4Ca + 2SO^4H^2 + 2H^2O + 2CO$$

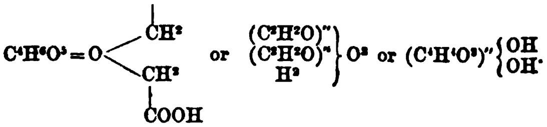
and

$$\underset{\text{Diglycollate.}}{C^4H^4O^5Ca} + 2SO^4H^2 = C^2H^4O^2 + SO^4Ca + SO^4H^2 + H^2O + 2CO.$$

A double salt of glycollate and chloride of calcium, $(C^2H^3O^3)^2Ca.CaCl^2 + 6H^2O$, is formed on leaving a highly concentrated mixed solution of the two salts to itself, or by boiling benzoglycollic acid with hydrochloric acid, neutralising the liquid filtered from benzoic acid with lime, and evaporating to a syrup. It forms large, transparent octohedral crystals, which do not alter in the air or over sulphuric acid, but give off 5 mol. water at 70°, the greater part of the remainder at 180°, and decompose at 200° (Jazukowitsch, *Zeitschr. Ch. Pharm.* 1864, p. 62).

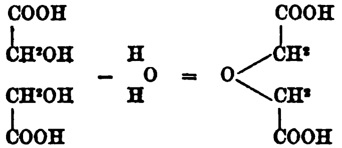
Butyroglycollic Acid. $C^6H^{10}O^4 = C^2H^3(C^4H^7O)O^3$.—The ethylic ether of this acid, $C^6H^{10}O^4.C^2H^5$, is produced by heating ethyl monobromacetate with potassium butyrate. It is a liquid insoluble in water, boiling at 205°–207°, and resolved by distillation with potassium hydrate into ethyl butyrate and potassium glycollate (Gal, *Bull. Soc. Chim.* [2] vii. 329).

Diglycollic Acid.



$$C^4H^6O^5 = O\begin{cases}CH^2-COOH\\CH^2-COOH\end{cases} \text{ or } \left.\begin{matrix}(C^2H^2O)''\\(C^2H^2O)''\\H^2\end{matrix}\right\}O^3 \text{ or } (C^4H^4O^3)''\begin{cases}OH\\OH.\end{cases}$$

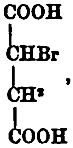
The constitutional formula of this acid is deduced from its mode of formation, viz. by abstraction of H^2O from two molecules of glycollic acid:



$$\begin{matrix}COOH\\|\\CH^2OH\\CH^2OH\\|\\COOH\end{matrix} - \begin{matrix}H\\O\\H\end{matrix} = O\begin{cases}CH^2-COOH\\CH^2-COOH\end{cases}$$

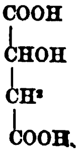
also by oxidation of diethylenic alcohol, $\left.\begin{matrix}(C^2H^4)^2\\H^2\end{matrix}\right\}O^3$.

Malic acid, with which it is isomeric, is formed by the action of alkalis on monobromosuccinic acid,



$$\begin{matrix}COOH\\|\\CHBr\\|\\CH^2\\|\\COOH\end{matrix}$$

, and has therefore the constitution



$$\begin{matrix}COOH\\|\\CHOH\\|\\CH^2\\|\\COOH.\end{matrix}$$

Diglycollic acid crystallises in imperfectly developed orthorhombic prisms of 107° 30', having their acute angles truncated by two faces, one of which makes an angle of 69° 58' with the faces of the prism. The plane of the optic axes is parallel to the smaller diagonal of the base of the prism (Friedel, *Jahresb.* 1863, p. 362). It melts at 148° and distils at 250°, for the most part undecomposed, a small portion being however resolved into glycollic acid, dioxymethylene, carbon dioxide, carbon monoxide, hydrogen, and carbon (Heintz, *Ann. Ch. Pharm.* cxxviii. 129).

Diglycollic acid heated with *hydriodic acid* is converted into glycollic and acetic acids, or into acetic acid alone, according to the proportion of hydriodic acid used;

$$C^4H^6O^5 + 2HI = C^2H^4O^3 + C^2H^4O^2 + I^2$$

and

$$C^4H^6O^5 + 4HI = 2C^2H^4O^2 + H^2O + 2I^2.$$

With fuming hydrochloric acid at 130°–140° it yields glycollic acid as chief product, with traces of acetic acid (Heintz, *Ann. Ch. Pharm.* cxxx. 257).

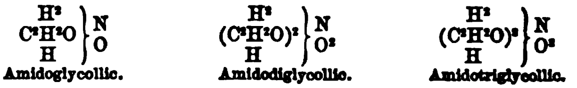
Neutral ammonium diglycollate, obtained by boiling the calcium salt with excess of ammonium carbonate, and evaporating the filtrate, is converted, by heating to 120°, into the acid salt $C^4H^5O^5(NH^4)$; and this latter heated to 250°, gives off 2 mol. water, and is converted into diglycollimide, $C^4H^5NO^3$, which melts at 142°, dissolves in about 57 pts. water at 14°, more easily in hot water, and crystallises from alcohol in splendid colourless needles (Wurtz, *Ann. Ch. Phys.* [3] lxix. 342).

For the preparation of *calcium diglycollate*, Heintz (*ibid.* cxliv. 91) recommends the following process: 1 pt. of monochloracetic acid is boiled with excess of quicklime, 3 pts. calcium chloride, and 10 pts. water, for ten hours in a flask provided with an upright condenser; and the liquid, diluted with boiling water, is quickly filtered, freed from excess of lime by carbon dioxide, evaporated to a thin syrup, and then mixed with 3 vol. alcohol. The liquid filtered from the calcium salt thus separated is again evaporated to dryness; the residue boiled with alcohol; and the solution mixed with absolute alcohol as long as a turbidity is thereby produced. The calcium salts precipitated by alcohol and washed therewith are then dissolved in boiling water, and the calcium diglycollate which first crystallises out is separated from the mother-liquor, and purified by washing with cold water. If the mother-liquors on further evaporation yield slender microscopic needles of the glycollate, together with transparent prisms of the diglycollate, the two salts may be separated by washing or levigation with a small quantity of hot water, which dissolves the glycollate and leaves the diglycollate: 10·5 grms. of chloracetic acid thus treated yield more than 8 grms. of calcium diglycollate and nearly 5 grms. of glycollate.

Ethyl diglycollate, $C^4H^5O^5.C^2H^5$, is prepared by heating the silver salt (obtained by precipitating the hot concentrated solution of the calcium salt with silver nitrate) with excess of ethyl iodide and anhydrous ether in a sealed tube in the water-bath; washing the silver iodide with ether; distilling off the ether and excess of ethyl iodide; volatilising the last portions of these ethers by heating to 100° in a stream of dry air; and finally distilling. It is a colourless liquid, boiling at 240°, heavier than water, having a faint odour, and slightly sweetish, somewhat burning taste. Boiling water dissolves and slowly decomposes it into diglycollic acid and alcohol. The same decomposition is instantly produced by boiling with alkalis and alkaline earths. By alcoholic ammonia it is converted into diglycollodiamide, $N^2(C^4H^4O^3)''H^4$ (Heintz, *Ann. Ch. Pharm.* cxliv. 95).

Amidoglycollic or Glycollamic Acids.

By the action of ammonia on monochloracetic acid, three amidated acids are produced, viz.,



$$\left.\begin{matrix}H^2\\C^2H^2O\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}\qquad\left.\begin{matrix}H^2\\(C^2H^2O)^2\\H\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}\qquad\left.\begin{matrix}H^2\\(C^2H^2O)^3\\H\end{matrix}\right\}\begin{matrix}N\\O^3\end{matrix}$$

Amidoglycollic. Amidodiglycollic. Amidotriglycollic.

The ethylic ethers of the same acids are produced by heating ethyl chloracetate with ammonia or ammonium carbonate (Heintz, ii. 905; *Ann. Ch. Pharm.* cxli. 355).

According to Ziegler (*Zeitschr. f. Chem.* [2] v. 659), a concentrated solution of amidoglycollic acid boiled with chloracetic acid yields the hydrochloride of amidodiglycollic acid; and in like manner, amidodiglycollic acid boiled with chloracetic acid yields the hydrochloride of amidotriglycollic acid; whereas by boiling glycollic acid with ammonia, neither amidoglycollic, amidodiglycollic, nor amidotriglycollic acid is obtained. Hence it may be inferred that in the preparation of these acids from chloracetic acid and ammonia, they are formed successively one from the other, an atom of hydrogen directly connected with nitrogen uniting at each step with the chlorine of the chloracetic acid, while the residue takes the place of the chlorine; thus,

$$\begin{aligned}C^2H^3ClO^2 &+ NH^3 &= C^2H^5NO^2.HCl\\C^2H^3ClO^2 &+ C^2H^5NO^2 &= C^4H^7NO^4.HCl\\C^2H^3ClO^4 &+ C^4H^7NO^2 &= C^6H^9NO^6.HCl\end{aligned}$$

Amidoglycollic acid, Glycollamic acid, Glycocine, or **Glycocoll,** $C^2H^5NO^2 = NH^2(CH^2COOH)$, is also formed by heating uric acid with saturated hydriodic acid to 160°–170° in sealed tubes:

$$C^5H^4N^4O^3 + 5H^2O = C^2H^5NO^2 + 3CO^2 + 3NH^3.$$

On opening the tubes, carbon dioxide escapes, and the solution, treated with lead hydrate and freed from dissolved lead by sulphydric acid, yields on evaporation colourless crystals of glycocine (Strecker, *Zeitschr. f. Chem.* [2] iv. 215).

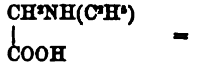
On the preparation of glycocine from hippuric acid, see Kraut a. Hartmann (*Ann. Ch. Pharm.* cxxxiii. 99). According to the same chemists, glycocine decomposed by *baryta-water* at 250° gives off ammonia, but no methylamine (compare ii. 903). Ammonia is also formed on heating it with hydriodic acid. When glycocine is heated with *lead dioxide and sulphuric acid*, the hydrocyanic acid produced, together with carbon dioxide and water, is in great part decomposed, so that the reaction may be represented by the equation, $C^2H^5NO^2 + O^3 = 2CO^2 + NH^3 + H^2O$.

Diglycocine hydrochloride, $2C^2H^5NO . HCl$, is deposited in needles on passing ammonia gas into the alcoholic solution of the neutral salt $C^2H^5NO^2 . HCl$.

Silver-glycocine, $C^2H^4AgNO^2$, is obtained by evaporating a solution of glycocine saturated while hot with silver oxide, over sulphuric acid: if the solution be evaporated by heat, silver is reduced; alcohol throws down from the solution a compound containing 3 at. silver to 4 mol. glycocine. When silver-glycocine is heated with ethyl iodide, 1 at. hydrogen is replaced by ethyl; but the product is decomposed by silver oxide, with reproduction of glycocine. Silver-glycocine distilled with barium hydrate gives off ethyl-methylamine, together with other bases. Boiled in excess with acetyl chloride and anhydrous ether, it yields silver chloride and aceturic acid, $C^4H^7NO^3$ (p. 30) (Kraut a. Hartmann, *loc. cit.*).

Glycocine nitrate, $C^2H^5NO^2 . NO^3H$, forms vitreous crystals belonging to the rhombic system, and having the axes $a : b : c$ (principal axis) in the ratio of 0·74972 : 1 : 0·06865 (Loschmidt, *Jahresb.* 1865, p. 349).

Ethylglycocine. $C^4H^9NO^2 = C^2H^4(C^2H^5)NO^2 =$

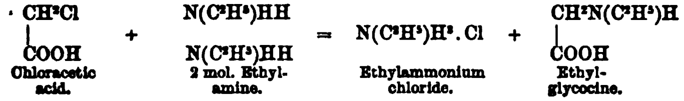


$$\begin{array}{l} CH^2NH(C^2H^5) \\ | \\ COOH \end{array} =$$

$$\left.\begin{array}{r} H . C^2H^5 \\ (C^2H^2O)'' \\ H \end{array}\right\} \begin{array}{l} N \\ O \end{array}$$

(Heintz, *Ann. Ch. Pharm.* cxxix. 27; cxxxii. 1; *Jahresb.* 1864, p. 362).—

Produced by prolonged boiling of chloracetic acid with ethylamine:



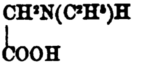
$$\begin{array}{c} CH^2Cl \\ | \\ COOH \\ \text{Chloracetic acid.} \end{array} + \begin{array}{c} N(C^2H^5)HH \\ \\ N(C^2H^5)HH \\ \text{2 mol. Ethylamine.} \end{array} = \begin{array}{c} N(C^2H^5)H^3 . Cl \\ \\ \text{Ethylammonium chloride.} \end{array} + \begin{array}{c} CH^2N(C^2H^5)H \\ | \\ COOH \\ \text{Ethylglycocine.} \end{array}$$

The product evaporated to dryness with excess of barium hydrate, and treated with boiling water, yields a solution containing ethylglycocine, together with a small quantity of the lead salt of ethylamidodiglycollic acid, and an insoluble residue B, consisting chiefly of the latter. On evaporating the solution A, and treating the residue with absolute alcohol, a small quantity of the lead salt B still remains undissolved, whilst the ethylglycocine passes into solution, together with other substances which interfere with the crystallisation. This solution is warmed with baryta-water (after the lead has been removed by hydrogen sulphide); the baryta is precipitated by cupric sulphate; and the filtrate is boiled with cupric hydrate, and mixed after evaporation with alcohol and ether. The cupric salt of ethylglycocine is thereby precipitated, and this when recrystallised from water and mixed in boiling solution with hydrogen sulphide, yields pure ethylglycocine.

Ethylglycocine crystallises from alcohol in indistinct laminæ; from the syrupy solution by evaporation over sulphuric acid, in small rectangular tables with truncated edges and summits. It has a sweetish, somewhat sharp, almost metallic taste, melts with decomposition above 160°, and deliquesces on exposure to the air. Its solution in hydrochloric acid evaporated at 100° leaves the hydrochloride $C^4H^9NO^2 . HCl$, which dissolves easily in water and in hot absolute alcohol, and crystallises from the aqueous solution by spontaneous evaporation in right rhombic prisms. The *platinochloride* $2(C^4H^9NO^2 . HCl) . PtCl^4 + 6H^2O$ crystallises from water in large orange-red monoclinic prisms. On mixing the solution of ethylglycocine with *mercuric chloride*, the compound $C^4H^9NO^2 . 2HgCl^2$ is formed as a crystalline precipitate, which crystallises from water in small rhombic prisms; and on dissolving these in hydrochloric acid, the syrupy compound $2(C^4H^9NO^2 . HCl) . HgCl^2$ is produced. *Cupric ethylglycocine* or *cupric ethylamidoglycollate*, $(C^4H^8NO^2)^2Cu + 4H^2O$, crystallises in oblique, apparently triclinic prisms, very soluble in water and alcohol, insoluble in ether. *Ethylglycocine hydriodide* is anhydrous, deliquescent, insoluble in ether, and crystallises like the hydrochloride.

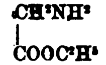
A compound isomeric with this hydriodide is obtained by heating glycocine with

1 mol. ethyl iodide is a sealed tube to 115°–120° (in a paraffin-bath). On evaporating the solution over sulphuric acid, rhombic crystals are obtained consisting of the compound $C^2H^4(C^2H^5)NO^2.HI$, which has an acid reaction, dissolves easily in water, alcohol, and ether, and when treated with silver oxide, is resolved, like a compound ether, into alcohol and glycocine (Schilling, *Ann. Ch. Pharm.* cxxvii. 97); hence, as pointed out by Kraut and Hartmann, the base $C^2H^4(C^2H^5)NO^2$ contained in it is not the ethylglycocine, or ethylamidoglycollic acid, obtained by Heintz, but the ethylic ether of amidoglycollic acid:



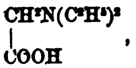
$$\begin{matrix} CH^2N(C^2H^5)H \\ | \\ COOH \end{matrix}$$

Ethylglycocine or Ethylamidoglycollic acid.



$$\begin{matrix} CH^2NH^2 \\ | \\ COOC^2H^5 \end{matrix}$$

Ethylic Amidoglycollate.



Diethylglycocine, $C^6H^{13}NO^2 = \begin{matrix} CH^2N(C^2H^5)^2 \\ | \\ COOH \end{matrix}$, is produced by boiling chloracetic acid with diethylamine. The product treated with hydrated lead oxide, freed from lead by hydrogen sulphide, and evaporated, yields diethylglycocine in deliquescent, rhombohedral crystals, very soluble in alcohol, subliming below 100°. Boiled with cupric hydrate, it yields the copper-compound $(C^6H^{12}NO^2)^2Cu + 4H^2O$, in small blue prismatic crystals. The *platinum-compound* $2C^6H^{13}NO^2.PtCl^4 + H^2O$ forms orange-red crystals (Heintz, *Ann. Ch. Pharm.* cxli. 217; *Jahresb.* 1866, p. 378; further, *Zeitschr. f. Chem.* [2] v. 152).

Methylglycocine. $C^2H^4(CH^3)NO^2$.—When glycocine is heated with methyl iodide to 100° for seven hours, sparingly soluble crystals separate, belonging to the rhombic system: they contain iodine, but their composition has not been ascertained. The mother-liquor yields transparent rhombic crystals easily soluble in water and alcohol, and consisting of the compound $C^4H^{10}NO^2I$, regarded by Schilling as the hydriodide of dimethylglycocine, $C^2H^3(CH^3)^2NO^2.HI$. Kraut and Hartmann, on the other hand, regard it as the methyl-iodide of monomethylglycocine. Its formation may be represented by the equation,

$$3C^2H^5NO^2 + 2CH^3I = (C^2H^5NO^2)^2HI + C^2H^4(CH^3)NO^2.CH^3I,$$

inasmuch as only one-third of the glycocine is converted into the methyl-compound, the rest being separated as diglycocine hydriodide, insoluble in absolute alcohol. The iodine-compound, when freed from alcohol and shaken up with silver chloride, is converted into the more stable chlorine-compound $C^2H^4(CH^3)NO^2.CH^3Cl$, which crystallises in white needles, and is not decomposed by water, but is resolved by silver oxide into glycocine and methyl alcohol, like the ethylic ether of glycollamic acid (Kraut a. Hartmann).

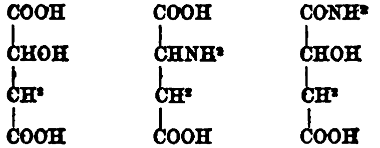
Phenylglycocine, $C^2H^4(C^6H^5)NO^2$, is produced, together with aniline hydrobromide, by the action of aniline on bromacetic acid. On dissolving the product in water, and evaporating, the phenylglycocine crystallises out first, and may be purified by pressure between paper and repeated crystallisation. It forms small indistinct crystals, melting at 110°, moderately soluble in water, sparingly in ether. The aqueous solution has an acid reaction, and dissolves the oxides of silver, lead, and zinc. The silver-compound decomposes partially in the cold, completely at the boiling heat, with formation of a silver speculum (Michaelson a. Lippmann, *Zeitschr. f. Chem.* 1866, p. 15).

Amidodiglycollic Acid. $C^4H^7NO^4 = NH\left\{\begin{matrix} CH^2COOH \\ CH^2COOH \end{matrix}\right.$ *Diglycollamidsäure.*—This acid is formed, together with glycocine and amidotriglycollic acid, by the action of ammonia on monochloracetic acid (ii. 905). It forms large, anhydrous, strongly acid crystals, having the form of rhombic prisms of about 129°, decomposes above 210°, dissolves in 41 pts. water at 5°, very easily in boiling water, is insoluble in alcohol and ether. It is bibasic. The *acid ammonium salt* $C^4H^6NO^4(NH^4)$, polymeric with glycocine, crystallises in large rhombic prisms of 95° 42′. The *silver salt* $C^4H^5NO^4Ag^2$ is thrown down from the ammonium salt by ammoniacal silver nitrate as a sandy white precipitate. The *monobaric salt* $C^4H^5NO^4Ba$ and the *bibaric salt* are gummy and uncrystallisable. The *cupric salt* $C^4H^5NO^4Cu + 2H^2O$, formed by decomposing the barium salt with cupric sulphate, is a blue crystalline powder, very slightly soluble in water. The *zinc salt* $C^4H^5NO^4Zn$, which is also very slightly soluble, is formed on boiling the acid with recently precipitated zinc carbonate (Heintz, *Ann. Ch. Pharm.* cxxii. 276; cxxiv. 297).

Amidodiglycollic acid also forms salts with the stronger acids. The *hydrochloride* $C^4H^7NO^4.HCl$ forms large, laminar, right rhombic prisms easily soluble in water, sparingly in alcohol. The *nitrate* $C^4H^7NO^4.NO^3H$ is a crystalline deliquescent mass. A solution of amidodiglycollic acid in 2 mol. sulphuric gradually deposits the neutral sulphate of amidodiglycollic acid, as a crystalline mass which is resolved by water or alcohol into the acid salt and free amidodiglycollic acid (Heintz, *Ann. Ch. Pharm.* cxxxvi. 213).

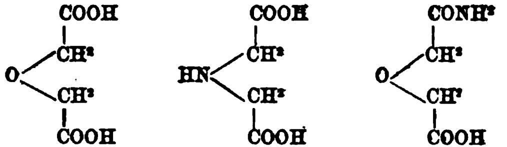
An acid isomeric with the preceding, which for distinction may be called **diglycollamic** (*Diglycollaminsäure*), is produced by treating diglycollimide (p. 649), with excess of warm baryta-water. The solution treated with carbonic acid, filtered, and evaporated, leaves an amorphous residue, from which hot alcohol extracts diglycollamic acid. The portion insoluble in alcohol is barium diglycollamate, $(C^4H^6NO^4)^2Ba + H^2O$, which, by covering the evaporated solution with a layer of alcohol, may be crystallised in small apparently oblique rhombic prisms This salt is neutral, moderately soluble in water, insoluble in alcohol and ether, decomposes above 145°, and is decomposed by prolonged boiling of its aqueous solution (more easily in presence of excess of baryta), giving off ammonia, and forming diglycollic acid, which is partly precipitated as barium salt. Diglycollamic acid separated from the barium salt by sulphuric acid forms unsymmetrical rhombic prisms of 84° 15. It is permanent in the air, moderately soluble in hot water, less in cold water and in alcohol, nearly insoluble in ether; melts above 125° to a mass which slowly solidifies and becomes opaque on cooling (Heintz, *Ann. Ch. Pharm.* cxxviii. 129; *Jahresb.* 1863, p. 364).

Amidodiglycollic and Diglycollamic acids are respectively isomeric with aspartic and malamic acids, which are amidated acids derived from malic acid. Aspartic and amidodiglycollic acids are bibasic; malamic and diglycollamic acids are monobasic. The constitutional formulæ of these acids, and their mode of derivation from malic and diglycollic acids, are indicated by the following formulæ:



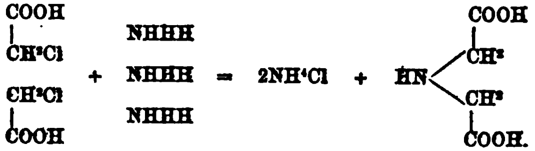
$$\begin{array}{ccc} COOH & COOH & CONH^2 \\ | & | & | \\ CHOH & CHNH^2 & CHOH \\ | & | & | \\ CH^2 & CH^2 & CH^2 \\ | & | & | \\ COOH & COOH & COOH \end{array}$$

Malic. Aspartic. Malamic.

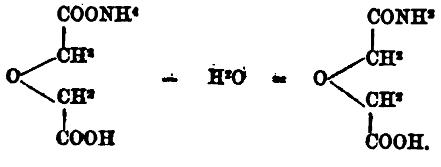


Diglycollic. Amidodiglycollic. Diglycollamic.

The formation of amidodiglycollic acid by the action of ammonia (3 mol.) on chloracetic acid (2 mol.) is represented by the equation:



Diglycollamic acid, being formed by addition of 1 mol. H^2O to diglycollimide, $C^4H^5NO^3$—which is itself produced from acid ammonium diglycollate by abstraction of $2H^2O$—may evidently be regarded as formed from the same acid ammonium salt by abstraction of 1 mol. H^2O; thus:



Ethyl-amidodiglycollic Acid. $C^6H^{11}NO^4 = NH\begin{cases}CH(C^2H^5)COOH\\CH^2COOH\end{cases}$.—The neutral ethylic ether of this bibasic acid,

$$C^{10}H^{19}NO^4 = C^6H^9(C^2H^5)^2NO^4 = NH\begin{cases}CH(C^2H^5)COO(C^2H^5)\\CH^2COO(C^2H^5)\end{cases},$$

is obtained by heating silver amidodiglycollate with ethyl iodide to 100°. It is a liquid soluble in ether, more soluble in alcohol than amidodiglycollic acid, distilling slowly in a stream of air at 200°–220°. By boiling with barium hydrate it yields a very sparingly soluble barium salt, from which, after separation of the barium by sulphuric acid, cupric ethyl-amidodiglycollate, $C^6H^9NO^4Cu$, may be prepared. It forms very soluble, blue, microscopic tables, which do not lose weight at 100° (Heintz, *Ann. Ch. Pharm.* cxlv. 214; *Zeitschr. f. Chem.* [2] v. 153).

Nitrosamidodiglycollic Acid. $C^4H^6N^2O^5 = C^4H^6(NO)NO^4$.—Formed, together with oxalic acid, by passing nitrous acid vapour into a solution of amidodiglycollic acid in nitric acid of sp. gr. 1·32. Separated from its barium salt by sulphuric acid, it crystallises from the syrupy solution in small pale yellow rectangular or six-sided tables, very much like the crystals of amidodiglycollic acid, but more soluble in water; it dissolves also in alcohol and ether, and melts without decomposition above 100°. Its calcium salt may be prepared by mixing a cold solution of amidodiglycollic acid in strong nitric acid with calcium nitrite till the liquid turns green, saturating the warm diluted solution with lime, evaporating to dryness, and treating the residue with alcohol. Calcium nitrosodiglycollamate then remains undissolved, which after recrystallisation from water has the composition $C^4H^4N^2O^5Ca + H^2O$; it is more soluble in cold than in hot water, nearly insoluble in alcohol, and crystallises from the syrupy aqueous solution in crusts which do not give off any water at 180°; the salt crystallised in a vacuum gives off 4 p. c. (½ mol.) water at 100°, and has then the composition of the salt dried at 160°. By treatment with ammonia and ammonium carbonate it is converted into ammonium nitrosamidodiglycollate; and this, by boiling with baryta-water, is converted into the barium salt, which by evaporation at the boiling heat is deposited in crystalline crusts containing $2C^4H^4N^2O^5Ba + H^2O$, and giving off their water (2·9 p. c.) at 180°–190°. The salt crystallised at lower temperatures has the composition $C^4H^4N^2O^5Ba + 2H^2O$, and becomes anhydrous at 125°. The *silver salt* $C^4H^4N^2O^5Ag^2$ crystallises from the warm dilute solution of the calcium salt, mixed with silver nitrate not in excess, in colourless sparingly soluble prisms, which detonate slightly when heated (Heintz, *Ann. Ch. Pharm.* cxxviii. 300).

Amidotriglycollic Acid. $C^6H^9NO^6 = N\begin{cases}CH^2COOH\\CH^2COOH\\CH^2COOH\end{cases}$. *Triglycollamidsäure* (Heintz, *Ann. Ch. Pharm.* cxxii. 269).—Formed, together with amidoglycollic and amidodiglycollic acids, by the action of ammonia on chloracetic acid:

$$3\begin{array}{l}CH^2Cl\\|\\COOH\end{array} + 4NH^3 = 3NH^4Cl + N[CH^2COOH]^3.$$

For the mode of separating it from the other two acids, see ii. 904. It forms small anhydrous crystals, of prismatic character, colourless, inodorous, and having only a faint acid reaction; they become white and opaque at 190°; fuse and decompose at a higher temperature. The acid dissolves in 747 pts. of water at 5°, somewhat more freely in boiling water, is insoluble in alcohol and ether. Hydrochloric acid precipitates it from the concentrated solution of its salts. The slightly ammoniacal solution of the acid gives with silver nitrate a white crystalline precipitate; with mercuric nitrate a precipitate which turns grey; cupric sulphate forms in the slightly acid solution of the ammonium salt an amorphous blue precipitate; lead acetate a white crystalline precipitate. The precipitate formed by barium chloride consists of regular six-sided microscopic tables, very soluble in hot water. Calcium chloride forms a precipitate only at the boiling heat (Heintz).

Amidotriglycollic acid is tribasic, but its monometallic salts have not been obtained. The *diammonic salt* $C^6H^7NO^6(NH^4)^2 + H^2O$ crystallises from an aqueous solution covered with a layer of alcohol, in needles very soluble in water; the *triargentic salt* $C^6H^6NO^6Ag^3$ is a white crystalline powder which detonates when heated (Heintz). The *dipotassic salt* $C^6H^7NO^6K^2 + H^2O$ crystallises slowly from a solution of 1 mol. amidotriglycollic acid and 1 mol. potassium carbonate mixed with alcohol, in long needles which give off their water at 110°. The *barium salt* $C^6H^7NO^6Ba + H^2O$, obtained by boiling 1 mol. of the acid with the corresponding quantity of barium hydrate or carbonate, forms sparingly soluble needles which give off their water at 120°, and decompose between 200° and 210°. The corresponding *lead salt* $C^6H^7NO^6Pb + 2H^2O$ crystallises in monoclinic prisms of 37° 30′ and 142° 30′, much truncated in the lateral direction, and with several hemidomes; soluble in about 30 pts. water; becomes anhydrous at 110°–120°, and decomposes at 210°. The *tribaric salt* $(C^6H^6NO^6)^2Ba^3 + 4H^2O$, produced by boiling the acid or its ammonium salt with excess of barium hydrate, forms thin nacreous quadratic plates, which give off their water at 180°. The *triplumbic salt* $(C^6H^6NO^6)^2Pb^3$, obtained by adding ammonium amidotriglycollate to an excess of basic lead acetate at the boiling heat, separates in opaque laminæ, which do not lose weight at 180° (W. Lüddecke, *Ann. Ch. Pharm.* cxlvii. 272; *Zeitschr. f. Chem.* [2] v. 153).

Triethylic amidotriglycollate, $C^6H^6NO^6.(C^2H^5)^3$, is obtained by heating the triargentic salt with ethyl iodide to 100° for six or eight hours; at higher temperatures it explodes. The ether obtained by distilling the filtered and dehydrated contents of the tube is a yellowish oily liquid having a fruity odour, distilling, with partial decomposition, between 280° and 290°, somewhat more soluble in cold than in hot water. It is decomposed by hydrochloric acid and by alkalis, with formation of amidotriglycollic acid. Its alcoholic solution, saturated with ammonia gas, gradually deposits crystals of amidotriglycollotriamide, $N(CH^2CONH^2)^3$ (Heintz, *Jahresb.* 1866, p. 397).

Amidotriglycollic acid subjected to dry distillation gives off water, ammonia, dimethylamine, carbon dioxide, probably mixed with carbon monoxide and a hydrocarbon, and leaves a carbonaceous residue. Nearly the same products are obtained by distilling the acid barium salt. Amidotriglycollic acid treated with *zinc* and *dilute sulphuric acid* is reduced to ethyl-amidodiglycollic acid: $C^6H^9NO^6 + 3H^2 = 2H^2O + C^6H^{11}NO^4$ (Lüddecke).

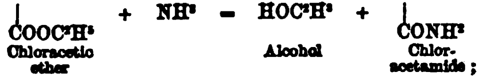
On the constitution of diglycollic, diglycollamic, and triglycollamic acids, see also Heintz (*J. pr. Chem.* [2] iii. 69, 120; *Chem. Soc. J.* [2] ix. 236; Kolbe, *J. pr. Chem.* [2] iii. 73; A. Claus, *ibid.* 123).

Glycollamides.

Glycollamide, isomeric with glycocine, is represented by the formula $\begin{array}{l}CH^2OH\\|\\CONH^2\end{array}$ or $\left.\begin{array}{c}H\\(C^2H^2O)''\\H^2\end{array}\right\}\begin{array}{l}O\\N\end{array}$.

Ethyl-glycollamide, $C^4H^9NO^2$ = $\begin{array}{l}CH^2OC^2H^5\\|\\CONH^2\end{array}$, is produced by leaving an alcoholic solution of ethylamine and ethyl glycollate to evaporate over sulphuric acid, and heating the syrupy residue to 120° in a current of air. It is syrupy, boils at 250°, becoming red at the same time, and is decomposed by alkalis, even in the cold, into ethylamine and glycollic acid. It is not altered by boiling with water. When evaporated with hydrochloric acid, it leaves a syrupy residue not containing glycollic acid (Heintz, *Ann. Ch. Pharm.* cxxix. 27).

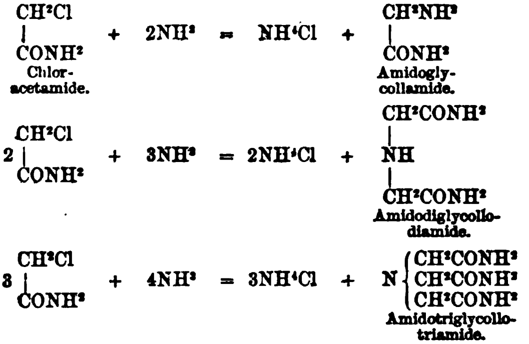
Amidoglycollamide, Glycocinamide, or **Glycocollamide.** $C^2H^6N^2O$ = $\begin{array}{l}CH^2NH^2\\|\\CONH^2\end{array}$ = $N\left\{\begin{array}{l}CH^2(CONH^2)\\H^2\end{array}\right.$ (Heintz, *Ann. Ch. Pharm.* cxlviii. 177; cl. 67; *Zeitschr. f. Chem.* [2] v. 161).—This compound is formed, together with amidodiglycollodiamide and amidotriglycollotriamide, by the action of alcoholic ammonia in large excess on ethylic monochloracetate, this ether being first converted into chloracetamide:



$$\underset{\text{Chloracetic ether}}{\begin{array}{l}CH^2Cl\\|\\COOC^2H^5\end{array}} + NH^3 = \underset{\text{Alcohol}}{HOC^2H^5} + \underset{\text{Chlor-acetamide}}{\begin{array}{l}CH^2Cl\\|\\CONH^2\end{array}};$$

Chloracetic ether Alcohol Chlor-acetamide;

and the latter, by prolonged action of the ammonia, into the three amides above mentioned; thus:



$$\begin{array}{c}CH^2Cl\\ |\\ CONH^2\\ \text{Chlor-}\\ \text{acetamide.}\end{array} + 2NH^3 = NH^4Cl + \begin{array}{c}CH^2NH^2\\ |\\ CONH^2\\ \text{Amidogly-}\\ \text{collamide.}\end{array}$$

$$2\begin{array}{c}CH^2Cl\\ |\\ CONH^2\end{array} + 3NH^3 = 2NH^4Cl + \begin{array}{c}CH^2CONH^2\\ |\\ NH\\ |\\ CH^2CONH^2\\ \text{Amidodiglycollo-}\\ \text{diamide.}\end{array}$$

$$3\begin{array}{c}CH^2Cl\\ |\\ CONH^2\end{array} + 4NH^3 = 3NH^4Cl + \begin{array}{c}N\left\{\begin{array}{l}CH^2CONH^2\\ CH^2CONH^2\\ CH^2CONH^2\end{array}\right.\\ \text{Amidotriglycollo-}\\ \text{triamide.}\end{array}$$

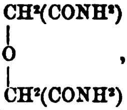
To prepare amidoglycollamide, the ethylic chloracetate is left in contact for some days with eight times its volume of saturated alcoholic ammonia; the mixture is then heated to 60° or 70° for 24 hours; the sal-ammoniac which crystallises out on cooling is separated by filtration; the free ammonia is left to evaporate over sulphuric acid; the solution obtained with the smallest possible quantity of water is mixed with alcoholic platinic chloride containing free hydrochloric acid, then with a quantity of ether equal to twice the volume of the liquid; and the precipitate which forms after standing for some time is washed on a filter with ether-alcohol. A small quantity of lukewarm water extracts from this precipitate the platinochloride of amidoglycollamide, whilst ammonium platinochloride and the platinochlorides of amidodiglycollodiamide and amidotriglycollotriamide remain undissolved. The solution yields by spontaneous evaporation large crystals of the platinochloride of amidoglycollamide, which may be freed from an adhering syrupy mass by treatment with dilute alcohol, and from any remaining portions of the three other platinum salts by picking out the crystals and recrystallising them from water.

Amidoglycollamide is also formed by heating glycocine with a large excess of alcoholic ammonia in a sealed tube to 155°–165°.

The *platinochloride of amidoglycollamide*, $2(C^2H^6N^2O.HCl).PtCl^4 + 2H^2O$, crystallises in monoclinic prisms with strongly developed oblique end-faces and predominant truncation of the acute prismatic edge; it is easily soluble in water, sparingly soluble in weak spirit, insoluble in strong alcohol and in ether; gives off its water of crystallisation at 105°, intumesces when heated, and yields a sublimate consisting chiefly of sal-ammoniac. Heated with a little hydrochloric acid and platinic chloride dissolved in dilute alcohol, it is converted into another platinum-compound, yellowish-red by transmitted, black-green by reflected light, easily soluble in water, insoluble in water mixed with an equal volume of alcohol. The same compound is formed as a secondary product in the preparation of the platinochloride of amidoglycollamide.

Hydrochloride of Amidoglycollamide, $C^2H^6N^2O.HCl$, is obtained by mixing the solution of the platinochloride in a small quantity of water with the quantity of sal-ammoniac required to convert the platinum into ammonium platinochloride; evaporating the filtrate in a vacuum; precipitating the filtered aqueous solution of the residue with alcohol and ether; washing the long thin needles thereby obtained with ether-alcohol; redissolving them in water; and leaving the solution to evaporate. The hydrochloride then separates partly in needles, partly in monoclinic prisms having their acute prismatic edges very much truncated. It is easily soluble in water, sparingly in alcohol, insoluble in ether; does not lose weight at 105°; melts when cautiously heated to a colourless liquid, which solidifies in the crystalline form on cooling; blackens at a higher temperature, boiling and giving off white vapours, and leaves a difficultly combustible, tumefied cinder. By boiling with barium hydrate, half the nitrogen is given off as ammonia, glycocine being at the same time produced. Its concentrated aqueous solution yields with platinic chloride the platinum salt above described; and with *auric chloride*, yellow microscopic right rhombic prisms with angles of about 114°, and sparingly soluble in alcohol.

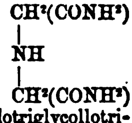
Amidoglycollamide itself has not been obtained quite pure, because its aqueous solution is easily decomposed by evaporation, or by boiling with aqueous alcohol, into glycocine and ammonia. It is separated from the hydrochloride by silver oxide, and the solution, freed from silver by hydrogen sulphide, leaves, when evaporated in a vacuum, a strongly alkaline syrup, which ultimately solidifies; the solid residue dissolves in the smallest quantity of cold water, but gives off ammonia even in the act of dissolution. If the residue be exhausted with absolute alcohol, in which glycocine is insoluble, the amidoglycollamide dissolves, forming an alkaline solution which deposits nothing on cooling, but when evaporated leaves amidoglycollamide, partly in microscopic rhombic tables, partly in slender needles, which deliquesce quickly on exposure to the air, impart a strong alkaline reaction to water and alcohol, and taste like a very weak alkaline-ley. With platinic chloride containing hydrochloric acid the solution yields the platinochloride above described. Amidoglycollamide absorbs carbon dioxide from the air, and its solution, saturated therewith, leaves on evaporation in a vacuum, a strongly alkaline syrup which solidifies in the crystalline form, effervesces with acids, and yields a solution which renders baryta-water turbid.

Diglycollodiamide, $C^4H^8N^2O^3 = N^2\left\{\begin{matrix}(C^4H^4O^3)''\\ H^4\end{matrix}\right. =$ 

$$\begin{array}{l}CH^2(CONH^2)\\ \vert\\ O\\ \vert\\ CH^2(CONH^2)\end{array}$$

, produced by the action of ammonia on ethyl diglycollate, crystallises from warm water in rhombic prisms of about 81°, combined with the end-face and two brachydomes (inclined to the principal axis at 64° and 80°); the prismatic faces are striated, and sometimes replaced by curved octohedral faces. Dissolves easily in boiling water (not quite without decomposition), less easily in cold water and in boiling alcohol, and is nearly insoluble in cold alcohol. It begins to give off ammonia at 115°, and melts at a stronger heat to a transparent colourless liquid, which solidifies in the crystalline form on cooling, but is resolved at a higher temperature into ammonia and diglycollimide: $C^4H^8N^2O^3 = NH^3 + C^4H^5NO^3$. By prolonged boiling of its aqueous solution, diglycollodiamide is converted into ammonium diglycollamate. It dissolves in dilute hydrochloric acid, but concentrated hydrochloric acid added to the solution throws down a crystalline precipitate of hydrochloride of diglycollodiamide, which gradually decomposes even during drying in a vacuum, leaving the pure diamide. The hydrochloric acid solution of diglycollodiamide leaves on evaporation a residue of sal-ammoniac and diglycollic acid (Heintz, *Ann. Ch. Pharm.* cxliv. 95).

Diglycollimide, $C^4H^5NO^3 = N\left\{\begin{matrix}(C^4H^4O^3)''\\ H\end{matrix}\right.$, is obtained by heating acid ammonium diglycollate, and passes over as a crystalline distillate, which, when purified by recrystallisation from hot alcohol, forms long silky prismatic crystals sparingly soluble in ether, easily soluble in hot water or alcohol, melting at a gentle heat, and subliming slowly at 100°. It crystallises without alteration from hot hydrochloric acid, is not precipitated by platinic chloride, but immediately gives off ammonia when treated with strong solution of potash. A crystalline silver-compound, $C^4H^4AgNO^3$, is obtained by precipitating a hot concentrated solution of diglycollimide with silver nitrate mixed with a little ammonia. When diglycollimide is supersaturated with warm baryta-water, and the liquid is treated with carbonic acid, then filtered and evaporated, an amorphous residue is left, from which hot alcohol extracts amidodiglycollic acid (p. 644) (Heintz, *Ann. Ch. Pharm.* cxxviii. 129; *Jahresb.* 1863, p. 364).

Amidodiglycollodiamide. $C^4H^9N^3O^2 = N^2\left\{\begin{matrix}[C^4H^3(NH^2)O^2]''\\ H^4\end{matrix}\right. =$ 

$$\begin{array}{l}CH^2(CONH^2)\\ \vert\\ NH\\ \vert\\ CH^2(CONH^2)\end{array}$$

(Heintz, *Zeitschr. f. Chem.* [2] v. 161).—Prepared, together with amidotriglycollotriamide, by heating ethyl chloracetate to 60°–70° with ammonia not in excess, or only in slight excess, expelling the excess of ammonia in the latter case by evaporation over sulphuric acid, and digesting the residue with absolute ether. The aqueous solution of the portion insoluble in ether generally deposits a certain portion of sal-ammoniac when evaporated in a vacuum, and the mother-liquor mixed with absolute alcohol yields a crystalline precipitate of the hydrochlorides of amidodiglycollodiamide and amidotriglycollotriamide, which must be washed with alcohol, redissolved in water, again precipitated with alcohol, and washed. The solution of these two hydrochlorides in cold water is mixed with silver oxide; the liquid filtered from the silver chloride is freed from silver by hydrogen sulphide; and the liquid filtered from the silver sulphide is evaporated in a vacuum over sulphuric acid. From the residue absolute alcohol extracts the amidodiglycollodiamide, while amidotriglycollotriamide remains undissolved. The two compounds may be purified by crystallisation from cold aqueous solution by spontaneous evaporation, the diamide also by recrystallisation from boiling alcohol.

the suspending wires T, multiplied by the angle of deflection of the coil. Hence the position of equilibrium of the coil, when the current is passing, is determined by the equation

$$CH.A \sin \beta = T\,(90^\circ - \beta)$$

or

$$CH = \frac{T\,(90^\circ - \beta)}{A.\sin \beta} \dots\dots (a).$$

And the simultaneous observation with the tangent-galvanometer gives

$$\frac{C}{H} = \frac{r}{2\pi} \tan \alpha \dots\dots (b).$$

The combination of these two equations, (*a*) and (*b*), gives both C and H in absolute measure. (For further details, see F. Kohlrausch, *Pogg. Ann.* [1869] cxxxviii. 1.)

Absolute Measurement of Electromotive Force.—The electromotive force of a galvanic battery, or other equivalent apparatus, may be defined as the quality in virtue of which it tends to do work by the transference of electricity from one point to another; and it may be expressed numerically by the amount of work done during the transfer of the unit quantity of electricity. Thus if W be the work done by the chemical or other forces of the battery, during the transfer of the quantity of electricity Q through the circuit, the electromotive force of the battery may be represented by

$$E = \frac{W}{Q} = \frac{W}{Ct},$$

the last expression being applicable when the electricity is transferred in the form of a current of uniform strength C lasting for the time t. Hence the electromotive force of a battery may also be said to be the work done when a current of unit strength is maintained for unit of time. The work may of course be of various kinds, as, for example, production of heat; work against gravity, as when weights are raised by an electromagnetic engine; work of acceleration against inertia; chemical work, as in a voltameter; magnetic and electrical work, as in an induction coil; but in the above formula it is supposed to be always expressed in absolute mechanical units.

But, just as electromotive force does work in a conducting circuit through the agency of the current which it produces, so, conversely, work done upon a conductor may give rise to electromotive force, and therefore to a current, if the conductor forms part of a closed circuit. This fact, coupled with the condition that the electromotive force developed when unit of work is expended per unit of time is to be taken as the unit of electromotive force, serves as the basis for the absolute measurement of electromotive force. The principles of the measurement will be easily understood from the following considerations.

If a current of the strength C′ circulate in a rectilinear conductor of length l placed at right angles to the lines of force in a uniform magnetic field of intensity H, every element dl of the current is subject to a force equal to

$$HC'dl$$

in a direction perpendicular to the current and to the lines of force. The resultant force acting upon the whole length l is therefore the sum of the forces acting upon the several elements of it, or

$$F = HC'l;$$

and if the conductor be displaced through the distance D perpendicularly to itself and to the lines of force, and in opposition to the force F, a quantity of work w will have been expended in producing the displacement which is expressed by

$$w = FD = HC'lD,$$

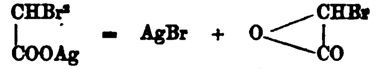
or, if the displacement take place with the constant velocity v and occupy unit of time, we may write

$$w = HC'lv.$$

If E be the electromotive force acting in the conductor when at rest, the work (in this case simply evolution of heat) done in unit of time by the electrical forces when the strength of the current is C′, will be

$$W = EC'.$$

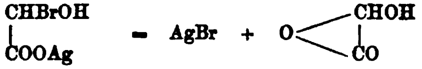
But the principle of the Conservation of Energy requires that, when an amount of work w is done upon the conductor by external forces, the equivalent of this work shall which gives up nothing to water, but when treated with potash or baryta-water is converted into a bromoglycollate: hence this yellow powder appears to contain bromoglycollide, formed according to the equation:



$$\begin{array}{l}CHBr^2\\ |\\ COOAg\end{array} = AgBr + O\left\langle\begin{array}{l}CHBr\\ |\\ CO\end{array}\right.$$

Silver Dibrom-acetate. Bromoglycollide.

This reaction renders it probable that silver bromoglycollate when heated will also yield, not an acid, but an anhydride. In fact, when this salt is heated in a sealed tube with anhydrous ether, a yellow powder is formed quite insoluble in ether, and the ether does not acquire any acid reaction, whereas if glyoxylic acid had been formed, it would have dissolved in the ether and rendered it acid. The yellow powder is likewise insoluble in water, but when heated with baryta, it immediately yields the decomposition-products of glyoxylic acid, viz. oxalate and glycollate. These results indicate that the yellow powder contains glyoxylide, $C^2H^2O^3$, from which glyoxylic acid is afterwards formed by addition of the elements of water. The formation of the glyoxylide is represented by the equation,



$$\begin{array}{l}CHBrOH\\ |\\ COOAg\end{array} = AgBr + O\left\langle\begin{array}{l}CHOH\\ |\\ CO\end{array}\right.$$

Silver Bromo-glycollate. Glyoxylide.

When dry silver bromoglycollate is heated in a sealed tube for several hours in the water-bath with absolute alcohol, a yellow powder is formed, together with a clear liquid which is perfectly neutral to dry litmus-paper, but instantly reddens the paper when moistened. On evaporating the alcohol, a neutral liquid is left perfectly soluble in water, and exhibiting when heated with lime-water the reactions of glyoxylic acid. This liquid is ethyl glyoxylate, formed according to the equations,

$$C^2H^2BrAgO^3 = AgBr + C^2H^2O^3$$

Silver Bromo-glycollate. Gloxylide.

and

$$C^2H^2O^3 + C^2H^5OH = C^2H^2O^4.C^2H^5$$

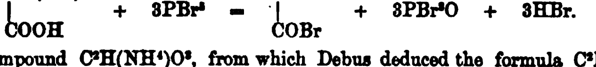
Glyoxylide. Alcohol. Ethyl glyoxylate.

This reaction seems to show that the body $C^2H^2O^3$ is an anhydride, and not glyoxylic acid; for in the latter case water would have been formed, and would have imparted an acid reaction to the liquid:

$$[C^2H^2O^3 + C^2H^5OH = C^2H(C^2H^5)O^3 + H^2O].$$

Glyoxylic acid (?).

A further argument in favour of the formula $C^2H^4O^4$ for glyoxylic acid is afforded by the behaviour of that acid with the pentachloride or pentabromide of phosphorus. Perfectly dry calcium glyoxylate distilled with phosphorus pentabromide yields hydrobromic acid, phosphorus oxybromide, and dibromacetyl bromide, which when dissolved in absolute alcohol, and treated with excess of water, yields ethyl dibromacetate:



$$\begin{array}{l}CH(OH)^2\\ |\\ COOH\end{array} + 3PBr^5 = \begin{array}{l}CHBr^2\\ |\\ COBr\end{array} + 3PBr^3O + 3HBr.$$

The compound $C^2H(NH^4)O^3$, from which Debus deduced the formula $C^2H^2O^3$ for glyoxylic acid, is regarded by Perkin a. Duppa as an amide which is converted into an ammonium salt when dissolved in water.

Dry sodium bromoglycollate heated to 120°–130° is gradually decomposed; and on treating the product with cold water, sodium bromide dissolves, and a white powder remains which dissolves in boiling water, forming a solution which exhibits the characters of glyoxylic acid. This white substance appears to be glyoxylide. It dissolves in ammonia, forming ammonium glyoxylate. Glycollide similarly treated yields glycollamide; and it might be expected that glyoxylide would also yield an amide; but the latter appears immediately to take up water, which converts it into an ammonium salt.

The following is a very characteristic reaction of glyoxylic acid: When a solution of calcium glyoxalate is mixed with aniline oxalate, and the liquid is filtered from calcium oxalate, a colourless solution is obtained, which when boiled, or even when left to itself for a few hours, deposits a bright orange-coloured precipitate (Perkin a. Duppa).

GOLD. For analyses of native gold from Siam, see Terreil (*Jahresb.* 1864, p. 825); from Bolivia: D. Forbes (*Phil. Mag.* [4] xxix. 122; *Jahresb.* 1865, p. 865); from Wales: D. Forbes (*Phil. Mag.* [4] xxxiv. 338; *Jahresb.* 1867, p. 972).

For the refining of gold—which is usually effected by fusing it with silver and treating the alloy with nitric or sulphuric acid (ii. 925)—F. B. Miller (*Chem. Soc. J.* [2] vi. 506) recommends the use of chlorine gas, which does not attack the gold even at high temperatures, but converts the silver and the other metals into chlorides. The gold is fused with borax in an earthenware crucible, previously dipped in borax solution to prevent it from being penetrated by the silver chloride. The crucible is closed by a well-fitting, but not luted cover, through which a small hole is bored. As soon as the gold is melted, a tobacco-pipe stem is inserted through this aperture to the bottom of the crucible, and chlorine gas, which need not be dried, is passed into the fused metal. By this simple method, as much as 100 ounces of gold may be refined at once. By means of a heated pipe-stem used as a pipette, a sample of the gold is taken out from time to time and its fineness tested in the usual way. When the operation is completed, the crucible is removed from the fire, left to cool till the gold solidifies, and the chlorides of the other metals, which still remain liquid, are poured into a mould so as to form them into a plate. The gold remaining in the crucible is remelted, and cast into ingots. To reduce the silver chloride, the plate is laid between two flat pieces of iron and immersed for 24 hours in water acidulated with sulphuric acid. The metal thus reduced still contains a little gold, which may be extracted from it by treatment with nitric acid, the gold being thereby separated however, not in globules, but in the flocculent state. It may also be separated by fusing the silver chloride with a small quantity of alkaline carbonate, whereby a certain quantity of metallic silver is separated, which reduces the gold completely. In this manner a regulus of argentiferous gold is obtained, together with silver chloride quite free from gold. By experiments carried out in the Royal Mint at Sidney, it has been found that the method above described is well adapted for practical use, and is not attended with greater loss than the methods generally practised.

Metallic gold dissolves when heated with strong sulphuric and a little nitric acid (the finely divided precipitated metal dissolving most readily), forming a yellow liquid, which when diluted with water, deposits the metal as a violet or brown powder. The solution also becomes covered with a shining film of reduced metal on exposure to moist air. On addition of hydrochloric acid or a metallic chloride, auric chloride is formed, no longer precipitable by water. A gold-solution exhibiting the same properties is formed by electrolysis of a mixture of 9 pts. sulphuric and 1 pt. strong nitric acid by means of a Grove's battery having a gold plate for the positive, and platinum for the negative pole. Gold is likewise attacked in the electrolysis of strong sulphuric acid alone, but immediately reduced again by the evolved hydrogen (Spiller, *Chem. News*, x. 178).

According to Nicklès (*Ann. Ch. Phys.* [4] x. 318), the easily decomposible higher metallic chlorides, bromides, and iodides are capable of dissolving gold. The ether-compounds of the perbromides and perchlorides (p. 596) are easily reduced by gold-leaf, with separation of chlorides and bromides insoluble in ether, and formation of a yellow ethereal solution which exhibits the characteristic reactions of auric chloride. The bromides and chlorides corresponding to the sesquioxides of manganese, cobalt, and nickel (?) dissolve gold even without the aid of ether; so likewise does a solution of ferric bromide at 50° or in sunshine, and the solution of plumbic tetrachloride, whereas a solution of ferric chloride remains unaltered in contact with gold. Free iodine in water does not act upon gold under ordinary pressure; but gold-leaf heated to 50° in a sealed tube with iodine and water is gradually dissolved; also, though more slowly, when the water is replaced by ether. An ethereal solution of iodine dissolves gold-leaf under ordinary pressure in very bright sunshine. Iodine in the nascent state also unites with gold. Ferric iodide, and the iodides corresponding to the higher oxides of manganese, bismuth, and other metals, are decomposed by gold, with formation of aurous iodide (it is sufficient to pour hydriodic acid upon the oxides and add gold-leaf). In presence of ether, hydriodic acid itself is decomposed, with formation of aurous iodide; gold-leaf immersed in ether is quickly dissolved on passing hydriodic acid into the liquid. Hydrobromic acid does not exhibit this reaction (Nicklès).*

A strip of metallic zinc introduced into a solution of gold in ammonium sulphide becomes coated with metallic gold (C. D. Braun, *Zeitschr. f. Chem.* [2] v. 308).

Auric Hydrate.—The light chestnut-brown compound obtained by precipitating dilute auric chloride with magnesia, and treating the precipitate with nitric acid, gives off at 100° a quantity of water corresponding to the formula $Au^2O^3 . 3H^2O$ or $Au'''H^3O^3$ (Wittstein, *Zeitschr. f. Chem.* [2] ii. 59).

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* Ferric oxide forms with ether and hydriodic acid a red solution which does not give a blue precipitate with potassium ferrocyanide till after standing for some time (Nicklès, *Compt. rend.* x. 479).

Gold-purple.—According to J. C. Fischer (*Dingl. pol. J.* clxxxii. 31, 129; *Jahresb.* 1866, p. 265), gold-purple in the air-dried state contains, as essential constituents, only metallic gold, stannic oxide, and water. Its formation takes place in two stages, as shown by the equations:

$$2AuCl^3 + 3SnCl^2 = Au^2 + 3SnCl^4$$

and

$$3SnCl^4 + 6H^2O = 3SnO^2 + 12HCl.$$

If the solutions are mixed in the requisite proportions (100 pts. gold to 90 pts. tin), the precipitate contains 1 mol. gold to 3 mols. stannic oxide. Any excess of gold remains in solution; but if the solutions are sufficiently dilute, an excess of stannous chloride renders the precipitate richer in stannic oxide; the proportion of the latter is likewise increased by addition of stannic chloride, although this compound has no influence on the formation of the true gold-purple.

Gold Chlorides.—Auric chloride, $AuCl^3$, is resolved at about 200° into metallic gold and aurous chloride, AuCl, and at higher temperatures into gold and chlorine. Nevertheless, auric chloride may be sublimed and obtained thereby in rather large crystals, even at a temperature higher than that at which it ordinarily decomposes—namely, by passing chlorine over gold-leaf heated to 300° in a tube; auric chloride is then formed, and condenses on the cooler parts of the tube in long needles. In this case the resolution (dissociation) of the trichloride into gold and chlorine is prevented by the tension of the atmosphere of chlorine by which it is surrounded (see CHEMICAL AFFINITY, p. 425) (Debray, *Compt. rend.* lxix. 984; *Zeitschr. f. Chem.* [2] vi. 87).

According to Prat (*Compt. rend.* lxx. 840; *Zeitschr.* [2] vi. 275), an intermediate chloride is formed by dissolving gold-sponge in a solution of the trichloride, or by heating the monochloride with the trichloride. By passing chlorine over any chloride of gold at a suitable temperature a volatile chloride may be obtained containing more chlorine than the trichloride (?).

GRAHAMITE. A pitch-black mineral resembling albertite, occurring in Ritchie County, Virginia. It is insoluble in alkalis and in alcohol, partially soluble in benzol and in ether, almost wholly in chloroform and carbon bisulphide; softens at about 200°, and contains 76·45 p. c. carbon, 7·82 hydrogen, 13·46 oxygen, and 13·46 ash (H. Wurtz, *Sill. Am. J.* [2] xlii. 420).

GRANATIN. This name is applied by R. Hermann (*Jahresb.* 1867, p. 996) to a mineral, hitherto regarded as serpentine, found near the mouth of the river Achtaragda in Eastern Siberia. It is massive, opaque, ash-grey with a tufaceous aspect, and uneven dull fracture; hardness = 3; sp. gr. = 2·66. According to Hermann's analysis, it is a mixture of 57·43 p. c. garnet and 42·57 serpentine.

GROPPITE. This mineral has been found by Descloizeaux in the form of greenish granules in the anhydrite of Modane in Savoy (*Bull. Soc. Géol. de France*, xxii. 25; *Jahresb.* 1865, p. 893).

GUAIACOL, $C^7H^8O^2$, has the composition of methyl-pyrocatechin, $C^6H^5(CH^3)O^2$, and is resolved by distillation with iodine, phosphorus, and water, into methyl iodide and pyrocatechin:

$$C^7H^8O^2 + HI = CH^3I + C^6H^6O^2.$$

Conversely it is formed by heating pyrocatechin in a sealed tube to 160°–170° with equivalent quantities of hydrate and methyl-sulphate of potassium:

$$C^6H^6O^2 + KHO + CH^3KSO^4 = C^7H^8O^2 + SO^4K^2 + H^2O$$

(Gorup-Besanez, *Jahresb.* 1867, p. 668; *Zeitschr. f. Chem.* [2] iv. 392).

Guaiacol occurs, together with creosol, $C^8H^{10}O^2$, in certain kinds of wood-tar creosote (p. 503). Rhenish beech-tar creosote treated with hydrochloric acid and potassium chlorate yields two compounds, tetrachloroguaiacone and tetrachlorocreosone, whose formation is represented by the equations:

$$\underset{\text{Guaicol.}}{C^7H^8O^2} + 10Cl = \underset{\substack{\text{Tetrachloro-}\\\text{guaiacone.}}}{C^7H^2Cl^4O^2} + 6HCl$$

and

$$\underset{\text{Creosol.}}{C^8H^{10}O^2} + 10Cl = \underset{\substack{\text{Tetrachloro-}\\\text{creosone.}}}{C^8H^4Cl^4O^2} + 6HCl.$$

They are separated by cold chloroform, in which tetrachloroguaiacone is insoluble. This compound forms lemon-yellow inodorous scales having a golden lustre, or a laminar crystalline mass. It is idioelectric, sublimes at about 180°, but is decomposed by rapid heating, with formation of copper-red needles and laminæ. It is nearly insoluble in cold water and alcohol, dissolves slowly in cold ether, easily in boiling alcohol or chloroform (Gorup-Besanes).

According to Marasse (*Ann. Ch. Pharm.* clii. 80), these compounds are formed, not from guaiacol and creosol, but from cresyl alcohol and phloryl alcohol existing in the creosote (p. 504).

GUANIDINE, CH^5N^3, or *Carbotriamine*, $\left.\begin{matrix}C^{iv}\\H^5\end{matrix}\right\}N^3$ (Hofmann, *Zeitschr. f. Chem.* [2] ii. 1073; iv. 721).—This base is formed: α. By the action of ammonia on chloropicrin:

$$CCl^3NO^2 + 3NH^3 = CH^5N^3.HCl + 2HCl + NHO^3.$$

It is easily prepared in large quantity by heating chloropicrin to 100° for several hours with a strong alcoholic solution of ammonia, exhausting the resulting saline mixture with anhydrous alcohol, which leaves the sal-ammoniac completely undissolved, and repeating this process once more with the guanidine hydrochloride dissolved in alcohol.

Guanidine is also produced: β. In small quantity by the action of ammonia at 150° on ethyl orthocarbonate:

$$C(C^2H^5)^4O^4 + 3NH^3 + H^2O = CH^5N^3.H^2O + 4C^2H^6O.$$

γ. Together with urea and other products, by the action of ammonia on carbonyl chloride (Bouchardat, *Compt. rend.* lxix. 961).—δ. By heating cyanamide in alcoholic solution with ammonium chloride:

$$CH^2N^2 + NH^4Cl = HCl + CH^5N^3$$

(Erlenmeyer, *Zeitschr. f. Chem.* [2] vii. 28).

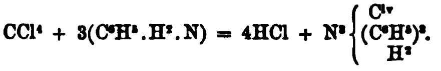
Guanidine Nitrate, $CH^5N^3.HNO^3$, is precipitated from a solution of the hydrochloride mixed with potassium nitrate, as a crystalline powder, and may be obtained by recrystallisation from boiling water, in sparingly soluble laminar crystals. Mixed with *silver nitrate*, it forms the crystalline compound $CH^5N^3.AgNO^3$. Moderately concentrated solutions of guanidine hydrochloride and *auric chloride* yield long needles of the gold salt, $CH^5N^3.HCl.AuCl^3$.

Dry guanidine hydrochloride dissolves easily in heated *aniline*, the solution giving off ammonia when boiled and solidifying on cooling. Water extracts from this product aniline hydrochloride, and leaves a compound which crystallises from alcohol in needles, does not dissolve in acids or in alkalis, and has the composition of melaniline, $CH^3(C^6H^5)^2N^3$, but differs altogether from it in properties. Toluidine acts upon guanidine hydrochloride in a similar manner.

Substituted Guanidines.

Erlenmeyer has obtained methyl-, phenyl-, and tolyl-guanidine by a process similar to that above mentioned for the production of guanidine itself, viz. by the action of cyanamide on the hydrochlorides of methylamine, phenylamine, and toluidine. The *methyl-guanidine* thus obtained does not differ perceptibly in its own properties or in those of its salts from methyluramine obtained by oxidising creatine or creatinine (iii. 1009), excepting in the platinochloride, which appears to differ somewhat in crystalline form from that of methyluramine.

Triphenyl-guanidine or **Carbo-triphenyl-triamine.** $C^{19}H^{17}N^3 = N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3.\\H^2\end{matrix}\right.$ —A base having this composition was first obtained by Hofmann (iv. 464) by the action of aniline on carbon tetrachloride:



$$CCl^4 + 3(C^6H^5.H^2.N) = 4HCl + N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3.\\H^2\end{matrix}\right.$$

Bassett (*Chem. Soc. J.* [2] iii. 31) obtained the same compound by the action of aniline on chloropicrin; and a base isomeric with this (at first however regarded as tricarbohexanilide, $C^{39}H^{36}N^6$) has been obtained by Merz a. Weith (*Zeitschr. f. Chem.* [2] iv. 513, 609; v. 583, 659) by the action of heat and of various desulphurating agents on sulphocarbanilide.

1. When sulphocarbanilide is distilled, carbon bisulphide and hydrogen sulphide are given off, while an amorphous vitreous mass remains, consisting of triphenylguanidine mixed with aniline. The decomposition is represented by the following equations:

$$\underset{\text{Sulphocarbanilide.}}{N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right.} = \underset{\text{Aniline.}}{N\left\{\begin{matrix}C^6H^5\\H^2\end{matrix}\right.} + \underset{\text{Sulphocarbanil.}}{N\left\{\begin{matrix}CS\\C^6H^5\end{matrix}\right.}$$

$$\underset{\text{Sulphocarbanilide.}}{N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right.} + \underset{\text{Sulphocarbanil.}}{N\left\{\begin{matrix}CS\\C^6H^5\end{matrix}\right.} = CS^2 + \underset{\text{Triphenylguanidine.}}{N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3\\H^2\end{matrix}\right.}$$

$$\underset{\text{Sulphocarbanilide.}}{N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right.} + \underset{\text{Aniline.}}{N\left\{\begin{matrix}C^6H^5\\H^2\end{matrix}\right.} = H^2S + \underset{\text{Triphenylguanidine.}}{N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3\\H^2\end{matrix}\right.}$$

The decomposition begins below the boiling point of aniline, and after heating for several hours to 160°, considerable quantities of triphenyl-guanidine are obtained. Carbanilide, $N^2(CO)''(C^6H^5)^2H^2$, when thoroughly dry, splits up in the same manner, yielding triphenyl-guanidine, together with aniline, carbon dioxide, and water. The decomposition is represented by equations precisely similar to the above, the sulphur in each being replaced by oxygen.

2. Triphenyl-guanidine is also produced, as a hydrochloride, when sulphocarbanilide is fused with lead chloride:

$$3N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right. + PbCl^2 = 2\left[N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3.HCl\\H^2\end{matrix}\right.\right] + CS^2 + PbS.$$

On exhausting the product with a little alcohol, adding a large quantity of water, and evaporating the filtrate, the pure hydrochloride crystallises out.

3. Ammonium sulphocyanate heated with excess of aniline yields successively sulphocarbanilamide (phenylsulphocarbamide), sulphocarbanilide (diphenylsulphocarbamide), and triphenyl-guanidine; thus:

$$N\left\{\begin{matrix}CS\\NH^4\end{matrix}\right. + C^6H^5.NH^2 = NH^3 + N^2\left\{\begin{matrix}CS\\C^6H^5\\H^3\end{matrix}\right.$$

$$N^2\left\{\begin{matrix}CS\\C^6H^5\\H^3\end{matrix}\right. + C^6H^5.NH^2 = NH^3 + N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right.$$

$$N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right. + C^6H^5.NH^2 = H^2S + N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3\\H^2\end{matrix}\right.$$

4. Triphenyl-guanidine is likewise produced by heating sulphocarbanilide with metallic copper, cuprous sulphide being also formed, together with greasy secondary products consisting of hydrocarbons, probably resulting from the decomposition of methylene formed in the first instance:

$$3N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right. + 3Cu^2 = 3Cu^2S + CH^2 + 2N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3.\\H^2\end{matrix}\right.$$

5. Together with phenylsulphocyanate, when sulphocarbanilide is heated to 160°–170° with concentrated hydrochloric acid (Merz a. Weith):

$$\underset{\text{Sulphocarbanilide.}}{N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right.} + HCl = \underset{\text{Aniline hydrochloride.}}{N\left\{\begin{matrix}C^6H^5\\H^2\end{matrix}\right..HCl} + \underset{\text{Phenyl sulphocyanate.}}{N\left\{\begin{matrix}CS\\C^6H^5\end{matrix}\right.}$$

and

$$\underset{\text{Sulphocarbanilide.}}{N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right.} + \underset{\text{Aniline hydrochloride.}}{N\left\{\begin{matrix}C^6H^5\\H^2\end{matrix}\right..HCl} = H^2S + \underset{\text{Triphenyl-guanidine hydrochloride.}}{N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3.HCl\\H^2\end{matrix}\right.}$$

6. Also when an alcoholic solution of iodine is poured into a boiling alcoholic solution of sulphocarbanilide (Hofmann, *Zeitschr. f. Chem.* [2] v. 671):

$$2N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right. + I^2 = N\left\{\begin{matrix}CS\\C^6H^5\end{matrix}\right. + N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3\\H^2\end{matrix}\right. + 2HI + S.$$

7. By the action of 1 mol. phosphorus trichloride on 3 mol. carbanilide and 3 mol. aniline (Merz a. Weith):

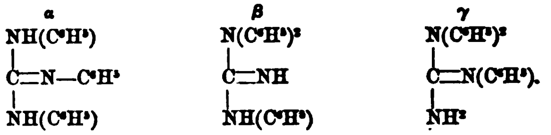
$$3N^2\left\{\begin{matrix}CO\\(C^6H^5)^2\\H^2\end{matrix}\right. + 3(C^6H^5.NH^2) + PCl^3 = 3N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3\\H^2\end{matrix}\right. + 3HCl + H^3PO^3.$$

8. By the action of 2 mol. PCl³ and 3 mol. CO² on 9 mol. aniline:

$$9(C^6H^5.NH^2) + 3CO^2 + 2PCl^3 = 3N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3\\H^2\end{matrix}\right. + 6HCl + 2H^3PO^3$$

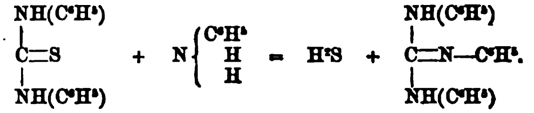
(Merz a. Weith, *Zeitschr. f. Chem.* [2] vi. 160).

Triphenyl-guanidine is susceptible of three isomeric modifications, viz.,



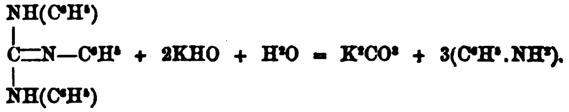
$$\begin{array}{ccc}\alpha & \beta & \gamma\\ NH(C^6H^5) & N(C^6H^5)^2 & N(C^6H^5)^2\\ | & | & |\\ C{=}N{-}C^6H^5 & C{=}NH & C{=}N(C^6H^5).\\ | & | & |\\ NH(C^6H^5) & NH(C^6H^5) & NH^2\end{array}$$

The base obtained by the methods above given is the α modification; this is shown for example by its formation from sulphocarbanilide and aniline; thus:



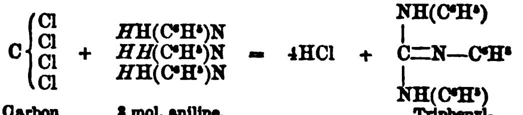
$$\begin{array}{c}NH(C^6H^5)\\|\\C{=}S\\|\\NH(C^6H^5)\end{array} + N\left\{\begin{matrix}C^6H^5\\H\\H\end{matrix}\right. = H^2S + \begin{array}{c}NH(C^6H^5)\\|\\C{=}N{-}C^6H^5.\\|\\NH(C^6H^5)\end{array}$$

Moreover, this base when heated with potash yields nothing but aniline and potassium carbonate, whereas the bases β and γ should yield diphenylamine and ammonia:



$$\begin{array}{c}NH(C^6H^5)\\|\\C{=}N{-}C^6H^5\\|\\NH(C^6H^5)\end{array} + 2KHO + H^2O = K^2CO^3 + 3(C^6H^5.NH^2).$$

Hofmann's carbotriphenyltriamine, obtained by the action of carbon tetrachloride, is regarded by Merz a. Weith as different from their triphenyl-guanidine; but the published descriptions of the two products do not exhibit any essential difference of properties. Moreover, Hofmann's reaction should yield a symmetrically constituted triamine identical in structure with that obtained from sulphocarbanilide by the methods above described. This may be seen from the following equation, in which the 4 hydrogen-atoms removed from the 3 aniline molecules to combine with the chlorine are printed for distinction in *italics*:



$$C\left\{\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right. + \begin{matrix}\mathit{H}H(C^6H^5)N\\ \mathit{HH}(C^6H^5)N\\ \mathit{H}H(C^6H^5)N\end{matrix} = 4HCl + \begin{array}{c}NH(C^6H^5)\\|\\C{=}N{-}C^6H^5\\|\\NH(C^6H^5)\end{array}$$

Carbon chloride. 3 mol. aniline. Triphenyl-guanidine.

α Triphenyl-guanidine is nearly insoluble in boiling water, dissolves in 22 pts. of absolute alcohol at 0°, much more easily in the hot liquid, and crystallises therefrom in white needles on cooling. The pure base melts at 143°, but the melting point is considerably lowered by the presence of small quantities of foreign substances. It is not volatile without decomposition. At 250° it gives off a liquid containing aniline, and from 280° upwards a gelatinous liquid smelling like bitter almond oil and solidifying to a hard vitreous mass, while a carbonaceous residue is left.

α Triphenyl-guanidine exhibits some remarkable colour-reactions with oxidising agents. A dilute solution of its hydrochloride, mixed with about 1½ pt. *potassium chlorate* and a little *hydrochloric acid*, acquires a yellowish and after a while a greenish colour;

and deposits dark-coloured flocks, which dissolve in alcohol with a fine violet colour; thin layers of this solution exhibit a fine garnet-red colour by transmitted light; thicker layers are opaque. When a larger quantity of potassium chlorate is used, the tints of the alcoholic solution incline more to red, afterwards to yellowish. Triphenyl-guanidine heated with a very large quantity of potassium chlorate deposits white flocks which become coloured by prolonged boiling, and form compact brick-red to madder-red particles, which are also dissolved by alcohol with violet-red colour. *Hypochlorites* and other oxidising agents react in the same manner with triphenyl-guanidine. *Chlorine-water* produces, even in very dilute solutions of the hydrochloride, an immediate whitish turbidity, which becomes flesh-coloured or lilac-coloured on heating the liquid. In concentrated solutions, or on agitation, the cloudy precipitate collects into flocks, probably consisting of chlorinated triphenyl-guanidine. The products obtained by all the processes above described exhibited exactly the same colour-reactions, down to the minutest detail.

Triphenyl-guanidine in alcoholic solution precipitates various metallic salts, *e.g.* ferrous and ferric salts, but not lead salts. In a stream of hydrochloric acid gas it becomes very hot and absorbs the gas, forming the *hydrochloride* $C^{19}H^{17}N^3.HCl$, which crystallises from water or alcohol with 1 mol. water. The *nitrate* $C^{19}H^{17}N^3.HNO^3$ forms nacreous laminæ, which, as well as the hydrochloride, have a distinct alkaline reaction. The *sulphate* $C^{19}H^{17}N^3.H^2SO^4$ crystallises from a hot solution containing free sulphuric acid in broad colourless needles having a strong acid reaction. The *oxalate* $C^{19}H^{17}N^3.C^2H^2O^4$ forms nacreous laminæ, also having an acid reaction, but only slightly soluble.

α Triphenyl-guanidine heated to 160°–170° in a sealed tube with a large excess of *carbon bisulphide* is converted into sulphocarbanilide and phenylsulphocyanate:

$$N^3[C^{iv}(C^6H^5)^3H^2] + CS^2 = N^2(CS)''(C^6H^5)^2H^2 + CNS(C^6H^5);$$

and when *hydrogen sulphide* is passed through it while fused at 170°, aniline distils over abundantly, and sulphocarbanilide remains behind:

$$N^3[C^{iv}(C^6H^5)^3H^2] + H^2S = N^2(CS)''(C^6H^5)^2H^2 + C^6H^5NH^2.$$

As carbon bisulphide, hydrogen sulphide, and triphenyl-guanidine are the final products obtained by the action of heat on sulphocarbanilide, it is easy to see that during this decomposition the carbon bisulphide and hydrogen sulphide will act upon the triphenyl-guanidine in the manner shown by the equations just given, thereby greatly diminishing the quantity of triphenyl-guanidine ultimately obtained; in fact, 90 p. c. of the sulphocarbanilide remains undecomposed (Merz a. Weith, *Zeitschr. f. Chem.* [2] vi. 72).

Triphenyl-guanidine is decomposed in a similar manner by heating it to about 250° and passing *carbon dioxide* through it, the products being carbanilide, aniline, and pungent vapours (perhaps carbanil). Heated with *water* to 170°–180°, it also yields carbanilide and aniline (Merz a. Weith).

An alcoholic solution of triphenyl-guanidine absorbs large quantities of *cyanogen gas*, and the saturated solution after some time deposits yellowish-white crystals of a base, $C^{21}H^{17}N^5$, which in contact with hydrochloric acid assumes a deep yellowish-red colour, due to the formation of a salt. This salt cannot, however, be isolated, being quickly resolved, with evolution of ammonia, into yellow crystals of oxalyl-triphenyl-guanidine, $C^{21}H^{15}N^3O^2 = N^3[C^{iv}(C^2O^2)''(C^6H^5)^3]$, formed according to the equation:

$$C^{21}H^{17}N^5 + 2H^2O = 2NH^3 + C^{21}H^{15}N^3O^2.$$

This last compound boiled with alcohol and hydrochloric acid yields aniline and diphenyl-parabanic acid, the latter body being ultimately resolved into aniline, oxalic acid, and carbon dioxide (Hofmann, *Berichte d. deutsch. chem. Gesellschaft*, 1870, p. 761).

A base having the composition $C^{21}H^{17}N^5$, but differing in properties from the above, is produced by the action of cyanogen on aniline. (See PHENYLAMINES.)

Tritolyl-guanidine, $C^{22}H^{23}N^3 = N^3[C^{iv}(C^7H^7)^3H^2]$, is obtained by reactions exactly similar to those which yield triphenyl-guanidine, *e.g.* by fusing sulphocarbotoluide (ditolyl-sulphocarbamide, $N^2(CS)''(C^7H^7)H^2$) with metallic copper, or by heating it alone or with hydrochloric acid. It dissolves in 13·5 pts. alcohol at 0°, more easily in hot alcohol or ether, and crystallises from alcohol in tufts of long satiny needles, resembling theine; very slightly soluble in boiling water. It melts at 123°, and usually solidifies to a transparent vitreous mass; leaves a carbonaceous residue when distilled. Its alcoholic solution has a strong alkaline reaction, and precipitates ferric, cupric, and lead salts.

The salts of tritolyl-guanidine crystallise with remarkable facility, and are on the whole much less soluble than those of triphenyl-guanidine. The *hydrochloride* $C^{22}H^{23}N^3.HCl + H^2O$ crystallises from cold alcohol by slow evaporation in large transparent prisms; from hot water in more tabular crystals. The *platinochloride* $C^{22}H^{23}N^3.HCl.PtCl^4$ forms slender yellow or orange-coloured needles, sparingly soluble in hot water. The *nitrate* $C^{22}H^{23}N^3.HNO^3$ crystallises on adding nitric acid to a hot solution of the base in aqueous alcohol, in white slender needles; from boiling water in prisms. Dissolves in 1,400 pts. water at 0°. The sulphate $(C^{22}H^{23}N^3)^2H^2SO^4$ crystallises from hot water in iridescent laminæ having a neutral reaction and moderately soluble in water (Merz a. Weith).

Tritolyl-guanidine is decomposed by carbon bisulphide and by hydrogen sulphide in the same manner as a triphenyl-guanidine. *Diphenyl-tolyl-guanidine* heated with carbon bisulphide yields as chief products, sulphocarbanilide and tolyl-sulphocyanate (Merz a. Weith):

$$N^3[C(C^6H^5)^2(C^7H^7)H^2] + CS^2 = N^2(CS)''(C^6H^5)^2H^2 + CNS(C^7H^7).$$

GUARANA or *Uarana*, the fruit of *Paullinia sorbilis*, has been analysed by Peckolt (*Jahresb.* 1866, p. 709). The seed-shells contain 2·443 p. c. caffeine; the shelled seeds, 4·813 p. c.; the pulp, 4·288 p. c.

GUM. Gum-arabic heated to 150° with 2 pts. of acetic anhydride swells up to a mass which, when washed with boiling water and then with alcohol, leaves a white amorphous insoluble powder, which is saponified by alkalis with reproduction of soluble gum. This substance is diacetyl-arabin, $C^6H^8(C^2H^3O)^2O^5$. If the gum be heated to 180° for five or six hours, with excess of acetic anhydride, triacety-arabin similar to the former is produced (Schützenberger a. Naudin, *Compt. rend.* lxviii. 814).

Ritthausen (*J. pr. Chem.* xcii. 321; *Jahresb.* 1867, p. 747) has obtained from the grain of rye a kind of gum soluble in dilute alcohol. It resembles vegetable mucilage, and is obtained by digesting rye-flour with cold alcohol of 50 p. c., and mixing the clear extract with a large quantity of strong alcohol. The ropy voluminous coagulum thereby separated dries up over sulphuric acid, after washing with strong alcohol, to a loose colourless mass, which (after deduction of ash) consists of $C^6H^{10}O^5$. When dried and finely pulverised, it forms with 25–30 pts. water, or with 30–40 pts. aqueous alcohol, a thickish solution difficult to filter, which dries up to a yellowish residue resembling gum-arabic. Cupric sulphate and potash form with the solution a light blue precipitate insoluble in excess of potash; lead acetate, neutral or basic, and mercurous nitrate do not precipitate it. The aqueous or alcoholic solution of the gum has no action on polarised light, but by prolonged boiling with dilute sulphuric acid it is converted into dextroglucose.

Chagual gum, a variety brought from St. Jago de Chile, resembles gum-senegal. The portion of it, amounting to about 75 p. c., which is soluble in water, has the composition $C^{12}H^{11}O^{11}$, is not thickened by borax, is precipitated by neutral lead acetate, but not by potassium silicate, and when treated with dilute sulphuric acid is completely converted into dextroglucose (Pribram, *Jahresb.* 1867, p. 747).

On the precipitation of dextrin gum by alcohol from solutions containing vegetable mucilage, see Günsberg (*Bull. Soc. Chim.* v. 526; *Jahresb.* 1863, p. 571).

GUMMIC ACID. This name was given by Reichardt to a crystalline acid, $C^6H^{12}O^{10}$, which he obtained by oxidising glucose with cupric oxide in alkaline solution (ii. 956). It has since been examined by Felsko (*Ann. Ch. Pharm.* cxlix. 356; *Zeitschr. f. Chem.* [2] v. 228), working under Reichardt's direction, who finds that the syrupy light yellow liquid which remains on evaporating a solution of the acid over calcium chloride, has the composition $C^6H^{14}O^{12}$; this he designates as *hydrated gummic acid* (*Gummisäurehydrat*), and represents by the formula $3HO.C^6H^3O^{10} + 6HO$ or $3H^2O.C^6H^{10}O^{10} + 6H^2O = \left.\begin{matrix}(C^6H^{10}O^7)^{vi}\\H^6\end{matrix}\right\}O^6 + 6aq.$, according to which it is a sexbasic acid. It has an intensely sour taste, mixes in all proportions with water and alcohol, turns the plane of polarisation to the left. It is precipitated directly by lime-water, and after neutralisation, by calcium chloride, the precipitate being soluble in acetic acid, insoluble in ammonia; ferric chloride produces, after addition of alcohol, a yellow-brownish precipitate. The acid easily reduces platinum and silver salts. The syrupy acid, after standing for a considerable time, deposits rhombic prisms of gummic anhydride, $C^6H^{10}O^{10}$, which dissolves easily in alcohol and water, and reacts like the acid. The solution is lævogyrate. The anhydride does not give off water below 110°; emits acid empyreumatic vapours between

110° and 120°; melts at 140°-150°; and blackens, with increased emission of empyreumatic vapours, between 160° and 190°.

Gummic acid forms crystallisable salts containing 4 and 6 atoms of univalent metal, 2 or 3 at. of bivalent metal: thus there are two sodium salts containing respectively $C^6H^{10}O^{13}Na^6$ + 2aq. and $C^6H^{10}O^{13}Na^4H^2$ + 2aq.; a sodio-potassic salt, $C^6H^{10}O^{13}Na^2K^2H^2$; and two barium salts containing $C^6H^{10}O^{10}Ba^3$ + 6aq. and $C^6H^{10}O^{10}.Ba^2H^2$ (Felsko).

Gummic acid has also been examined by A. Claus (*Zeitschr. f. Chem.* [2] v. 152), according to whose analysis it is a bibasic acid, $C^3H^4O^5$, identical or isomeric with oxymalonic acid. Its barium and calcium salts have the composition $C^3H^2O^5Ba$ and $C^3H^2O^5Ca$. Gummic or oxymalonic acid is not, however, the chief product of the oxidation of glucose by alkaline cupric solutions, being formed, indeed, only in small quantity, together with oxalic, formic, and acetic acids, and the gum obtained by Reichardt.

Oxygummic acid, $C^4H^{10}O^{11}$, produced by oxidation of gummic acid, is described in vol. iv. p. 312.

GUMMIDES. See GLUCOSIDES (p. 636).

GUN-COTTON. Pelouze a. Maurey (*Ann. Ch. Phys.* [4] iii. 186) assign to this substance the formula $C^{24}H^{36}O^{18}.5N^2O^5$; Blondeau (*Compt. rend.* lxi. 378) gives the formula $C^{24}H^{40}O^{20}.5N^2O^5$. Abel, however (*Phil. Trans.* 1866, p. 269; 1867, p. 181; *Chem. Soc. J.* [2] v. 310, 505), has shown, by a series of very carefully conducted experiments, that when Lenk's directions for the cleansing and nitration of the gun-cotton are exactly carried out, uniform products are obtained, whose composition, with the exception of slight variations due to admixtures to be presently noticed, is represented by the formula of trinitrocellulose, $C^{12}H^{14}O^7.3N^2O^5$ or $C^6H^7(NO^2)^3O^5$ (iv. 777). This result, deduced from numerous analyses, is also in accordance with the increase of weight which the cotton undergoes by nitration. The slight differences between the observed results and those required by the formula of trinitrocellulose are due partly to the presence of a small quantity (0·75 to 1 p. c.) of a yellow acid nitro-compound soluble in alcohol, which is produced by the action of the nitric acid on foreign substances still present in the purified cotton, and partly to the presence of 1 to 1·5 p. c. of the lower nitro-derivatives of cellulose. (See PYROXYLIN, iv. 782.)

Well-prepared gun-cotton exposed to diffused daylight or direct sunshine gradually gives off a little gas, but without undergoing any essential alteration. Pelouze a. Maurey found indeed that gun-cotton undergoes rapid decomposition even at temperatures below 100°, giving off nitrous vapours and sometimes exploding; but according to Abel, neither trinitrocellulose nor the less nitrated products just mentioned are affected when pure by a temperature near 100°, and the easy decomposibility of gun-cotton sometimes observed is due to the presence of nitro-derivatives of foreign organic substances (the incrusting matter of the cellular tissue), which when heated, quickly decompose, with formation of free acid. This tendency to decomposition may be arrested by impregnating the finished gun-cotton with sodium carbonate. Gun-cotton may be preserved for any length of time by immersing it in water, or saturating it with moisture sufficiently to render it uninflammable. In this condition it is less dangerous than gunpowder can be rendered by any process whatever, may be transported as safely as raw cotton, and is less prone than the latter to gradual deterioration by mouldiness and putrefaction.

The normal firing temperature of gun-cotton is about 150°, but under peculiar circumstances it may take fire at 136°, or when very loose masses are slowly heated, not till 205°. When the temperature is very gradually raised, the gun-cotton decomposes without taking fire, and is converted into a brown non-explosive substance (Abel). According to W. L. Scott (*Bull. Soc. Chim.* [2] ix. 383), gun-cotton explodes instantly in contact with the alkali-metals (but not with their amalgams) even when all friction is avoided. Other metals do not act in this way; pulverised arsenic however induces the explosion on percussion.

On the explosion of gun-cotton under the influence of detonating substances, such as fulminating silver and mercury, chloride of nitrogen, &c., see COMBUSTION (pp. 486–488).

GUNPOWDER. Abel, in connection with his experiments on gun-cotton (PYROXYLIN, iv. 779), has also examined the behaviour of gunpowder when heated in rarefied air. When small quantities (4 grains) under an air-pump receiver exhausted to a pressure of 15 to 51 millim., are touched with a fine platinum wire heated to redness, the grains nearest to the wire fuse, give off sulphur-vapours with ebullition, and at last take fire, scattering at the same time the rest of the unignited powder. Under a pressure of 76 millim. complete ignition takes place after about four seconds. The same phenomena are exhibited in an equally rarefied atmosphere of nitrogen or of oxygen; in the latter case the combustion is somewhat more brilliant. After combustion under very low pressure (below 38 millim.), the atmosphere of the combustion-chamber was always found to contain nitrous acid, and a sulphuretted compound having an odour of horseradish (*Proc. Roy. Soc.* xiii. 204). Similar results have been obtained by Heeren (*Dingl. pol. J.* clxxx. 286).

The products of the combustion of gunpowder under different circumstances have recently been examined by Fedorow (*Zeitschr. f. Chem.* [2] v. 12), who finds, in accordance with Craig (*Dingl. pol. J.* clxi. 462), but contrary to Karolyi (iv. 958), that these products vary in composition according to the mode of combustion. The powder-residue was prepared by firing a pistol within a glass tube 4 feet long, and by firing a 9-pounder copper cannon, using 3 pounds (Russian) of powder for each charge.

Composition of the Powder and of the Charcoal contained in it.

Powder.		Charcoal.	
Potassium Nitrate . . .	74·175	Carbon	72·5
Charcoal	14·835	Hydrogen	2·9
Sulphur	9·890	Oxygen	22·3
Water	1·100	Ash	2·3
	100·000		100·0

The residue was dissolved in water, the carbon and sulphur separated by filtration, and the filtrate agitated for several days with cadmium carbonate. The amount of sulphur in the potassium sulphide was calculated from the cadmium sulphate; the potassium hyposulphite was determined by precipitation with silver nitrate; the potassium sulphocyanate was estimated by the calorimetric method (Bunsen's); the carbonate by precipitating with manganese chloride and weighing the resulting manganic oxide, Mn^2O^3. The amount of potassium nitrate was calculated from the difference. The following results are the mean of several closely agreeing analyses:

Composition of Powder-residue calculated on 100 pounds of dry substance.

	Blank cartridge with:				Cannon-shot with 3-lb. charge	
	0·75 grm.		1·5 grm.			
K^2SO^4 . .	48·25	47·61	40·83	43·28	15·00	15·15
K^2CO^3 . .	23·44	24·13	30·96	31·90	37·00	36·20
$K^2S^2O^3$ . .	16·53	17·03	19·32	17·74	8·28	7·44
K^2S . .	0·97	0·54	2·49	1·67	38·18	39·55
KNO^3 . .	5·81	5·66	2·79	1·73	—	—
KCNS . .	0·54	0·54	0·56	0·56	0·33	0·33
S . . .	4·38	4·49	3·05	0·22	0·09	0·09
C . . .	4·08			2·90	—	1·02
Sand, CuO .	—	—	—	—	0·82	0·22
$(NH^4)^2CO^3$	traces				—	—

These analyses show decidedly that an increase of the charge is attended with a more complete combustion of the powder. The higher the pressure attending the explosion, the smaller is the quantity of undecomposed powder ($KNO^3 + C + S$) in the residue, and the greater the amount of potassium sulphide and carbonate in this residue, the sulphate diminishing in the same proportion. At high pressures the quantity of hyposulphite likewise diminishes. Retarded combustion, such as may be obtained by admixture of fatty matter with the powder, acts in the same manner as increased pressure. With a blank charge of 1·5 grm. of a mixture of 100 pts. meal-powder and 0·5 pt. stearic acid, a residue was obtained containing

K^2SO^4	$K^2S^2O^3$	K^2CO^3	K^2S	KCNS	C	S	
31·57	22·25	39·09	2·01	0·74	4·02	0·32	= 100.

The proportion of hyposulphite was therefore increased, and that of sulphate diminished.

In the experiments with the cannon, 100 pts. of anhydrous powder yielded 49·61 pts. of dry residue, whence it may be calculated that 1 grm. of powder would yield in this case 0·039 grm. aqueous vapour, and 258·7 c.c. gases (= 82·6 c.c. N + 162·1 c.c. CO^2 + 14 c.c. SO^2 and O). Nearly all the carbon was therefore converted into CO^2.

The preceding results lead to a theory of gunpowder different from that deduced from the experiments of Bunsen a. Schischkoff (ii. 958).

In the combustion of gunpowder several successive reactions take place. First the sulphur takes fire and potassium sulphate is formed; then the excess of oxygen burns the carbon to CO^2, which escapes with the nitrogen, while the excess of carbon reduces the potassium sulphate, forming potassium carbonate, hyposulphite, and free carbon dioxide (or monoxide); thus:

$$\text{I. } 2KNO^3 + S + C = K^2SO^4 + N + CO^2.$$

$$\text{II. } 2K^2SO^4 + C^3 = K^2S^2O^3 + K^2CO^3 + CO^2.$$

If the proportion of sulphur in the powder does not correspond with the normal composition $2KNO^3 + S + 3C$, as in Russian powder or in the sporting powder used in the experiments of Bunsen and Schischkoff, K^2CO^3 is formed in the first stage of the reaction as well as K^2SO^4.

In combustion in an open tube, the two reactions indicated by the above equations are the only ones that take place; but in combustion under pressure the free carbon exerts a further action on the hyposulphite; thus:

$$\text{III. } 2K^2S^2O^3 + C^3 = 3CO^2 + 2K^2S + S^2.$$

In this case also the free sulphur may act upon the potassium carbonate formed as in equation II. The hyposulphite is also decomposed at a high temperature. The sulphur acts upon the potassium carbonate essentially in the manner shown by the equation:

$$\text{IV. } 4K^2CO^3 + S^4 = K^2SO^4 + 3K^2S + 4CO^2.$$

Brugère (*Compt. rend.* lxix. 716) describes a kind of gunpowder prepared by mixing 54 pts. ammonium picrate with 46 pts. nitre. In the combustion of this powder the whole of the charcoal is burnt, and the residue consists entirely of potassium carbonate:

$$C^6H^2(NO^2)^3O.NH^4 + 2KNO^3 = 5CO^2 + 3N^2 + 3H^2 + K^2CO^3.$$

The volume of gas produced by the explosion is about 2½ times as great as that which is formed by the combustion of an equal weight of ordinary gunpowder. The new powder takes fire when touched with a burning body, but not by percussion. At 150° it assumes an orange-red colour, but undergoes no further alteration; at 190° the ammonium picrate begins to volatilise; at 300° the nitre melts, and at 310° the powder explodes. By prolonged contact with water it is resolved into potassium picrate and ammonium nitrate.

White Gunpowder.—This name is applied to an explosive material for fire-arms and for blasting, invented by E. Schultze (*Dingl. pol. J.* clxxv. 453), and consisting of nitrated woody fibre impregnated with salts rich in oxygen. To prepare it, finely divided wood or sawdust is first freed from acids and soluble substances by boiling it with a weak solution of sodium carbonate, and washing in running water, then dried, exposed to a current of steam to separate albuminous substances, again washed, bleached with chlorine, and finally washed, first with cold, then with hot water, and dried. The woody fibre thus purified is nitrated by maceration for some hours in a mixture of nitric and sulphuric acids, then washed with weak alkaline ley and with water, and dried. The product is a feebly explosive material which leaves a considerable carbonaceous residue when burnt; in this state it may be preserved and transported with safety. When required for use, it is steeped in a solution of potassium nitrate or of mixed potassium and barium nitrates, and dried at 32°–44°. This powder is said to be considerably more powerful than ordinary gunpowder as a blasting agent, and to produce little or no smoke; but it does not appear to be well adapted for fire-arms.

Respecting other explosive mixtures proposed as substitutes for gunpowder, see *London Journal of Arts*, 1864, pp. 29, 37; *Chem. News*, xi. 19; *Dingl. pol. J.* clxxii. 229, 236; clxxxii. 248, 251, 344; *Bull. Soc. Chim.* [2] ii. 391; v. 234; *Jahresb.* 1864, p. 795; 1866, p. 859; also Richardson and Watts's *Chemical Technology*, pt. iv. 435; pt. v. p. 385). Respecting the methods of estimating the force of gunpowder, see the last-mentioned work, pt. iv. p. 474.

GUTTA-PERCHA. The alterations which this substance undergoes in course of time have been carefully studied by W. A. Miller (*Chem. Soc. J.* [2] iii. 273). These alterations depend upon oxidation (ii. 962), which takes place especially when the gutta-percha is exposed to light and to the alternate action of air and water. Gutta-percha kept under pure water or sea-water retains its original properties for a long time; but if exposed in sunshine to the alternate action of air and water, it gradually increases in weight, becomes brittle, resinous, more soluble in alcohol and in dilute alkalis. Pure milk-white gutta-percha, perfectly soluble in benzol, ether, and carbon bisulphide, has the composition of a hydrocarbon, $C^{20}H^{32}$. Heated to 100° it softens and gradually takes 4·4 p. c. oxygen, becoming brown, resinous, and brittle; the oxidised portion is insoluble in benzol. Commercial gutta-percha, such as is used for the manufacture of cables, becomes liquid at 100°, and contains, together with the pure hydrocarbon and mechanically enclosed water, a considerable quantity of the resinous oxidation-product, as shown by the following analysis:

Hydrocarbon	Resin	Woody fibre	Water	Ash	
79·70	15·10	2·18	2·5	0·52	= 100.

After drying at 100° it exhibited the composition A; the oxidised portion soluble in alcohol had the composition B; the portion soluble in benzol, and precipitable therefrom by alcohol, had the composition C:

	Carbon	Hydrogen	Oxygen	
A . . .	84·66	11·15	4·19	= 100.
B . . .	76·15	11·16	12·69	= 100.
C . . .	87·22	12·04	0·74	= 100.

Commercial gutta-percha, if excluded from light, may also be kept for months or even years under water or in air; but when it is exposed to light in the open air, the portions on which the light falls quickly assume the composition above given.

H

HÆMATEÏN. See Hæmatoxylin (*infra*).

HÆMATIN. See Blood (p. 355).

HÆMATOÏDIN. This substance, originally found in blood and afterwards in bile (iii. 3), is most easily obtained, according to Hulm (*Bull. Soc. Chim.* [2] viii. 60), from the *Corpus luteum* of the cow. According to Piccolo a. Lieben, however, the dichroic crystals obtained from the latter source are not identical with hæmatoïdin. These chemists also consider it most probable that hæmatoïdin is identical with bilirubin, and propose to designate the new substance from the *Corpus luteum* as luteohaematoïdin or haemolutein (p. 497). Jaffé (*Jahresb.* 1862, p. 537) finds that hæmatoïdin (from the brain of an apoplectic patient) exactly resembles bilirubin in its reaction with nitric acid, becoming first green, then blue, violet, &c.

HÆMATOXYLIN. $C^{16}H^{14}O^{6}$.—A solution of this substance, or paper saturated with it, is recommended by Wildenstein (*Zeitschr. anal. Chem.* ii. 9) as a test-paper, especially for the detection of ammonia, the fixed alkalis, alkaline earths, and certain metals (iii. 5). Swedish filtering paper thus prepared has a yellowish colour when dry, and is coloured red, violet, or violet-blue by the smallest trace of an alkali.

As hæmatoxylin reduces silver salts, it may be used, like pyrogallic acid, for developing photographic pictures. A solution for the purpose may be prepared with 0·5 pt. hæmatoxylin, 80 pts. distilled water, and 22 pts. acetic acid: a little glycerin may also be advantageously added (Tabensky, *Zeitschr. f. Chem.* [2] v. 386).

Haematein may be quickly prepared by passing air containing ammonia, by means of an aspirator, into a bottle containing hæmatoxylin suspended in water, the delivery-tube terminating just above the surface of the liquid: by this arrangement, an excess of ammonia is avoided, which would produce a brown amorphous substance. When a considerable quantity of hæmatoxylin is used, it may be simply drenched with ammoniacal water. The process yields a solution having a fine violet colour, and forming with acid ammonium sulphite a precipitate soluble at the boiling heat (Tabensky).

According to Schützenberger a. Paraf (*Jahresb.* 1862, p. 495), the violet solution of hæmatoxylin in ammonia is decolorised by heating to 100° for 48 hours in an exhausted tube, a colourless pasty mass being formed, which the authors designate as haematinamide; on exposure to the air it quickly takes up oxygen, and turns violet. It is slightly soluble in water, easily in alcohol, ether, and hydrochloric acid; and is precipitated from the latter by ammonia in white flocks.

HÆMIN.
HÆMOGLOBIN. } See Blood (pp. 352, 356).

HÆMOLUTEIN. See Corpus Luteum (p. 497).

HAGEMANNITE. A fluoride occurring at Arksutflord in Greenland, together with cryolite and pachnolite. It is opaque, has an ochre-yellow or wax-yellow colour, and uneven fracture; hardness = 3 to 3·5; sp. gr. 2·59 to 2·60. Contains:

Al	Fe	Ca	Mg	Na	F	Si	H^2O	Insol.
12·06	5·96	11·18	2·30	8·45	40·30	7·79	10·44	1·08

(Shepard a. Hagemann, *Sill. Am. J.* [2] xli. 119).

HEAT. Thermometry.—A convenient form of *air-thermometer*, for the approximate measure of temperatures above 300°, has been contrived by Berthelot (*Ann. Ch. Phys.* [4] xiii. 144, and xv. 413). It consists of a cylindrical bulb of glass or silver, with thin sides, of about 4 cubic centim. capacity, communicating at the upper end with a capillary tube of uniform bore, about 1·2 metre long and 0·2 mm. in diameter. At a distance from the bulb of about 200 mm. this capillary stem is bent so as to become horizontal, and at about 250 mm. further on it is bent downwards at a right angle, and, after proceeding vertically downwards for a length of about 730 mm., it is again bent up, and terminates in a wide open bulb. A double graduation is attached to the vertical part of the stem: on one side a scale of millimetres, and on the other a scale of thermometric degrees. These two scales are both divided upon a flat strip of wood, which is supported so as to be capable of being moved a short distance up or down the stem, and then clamped in any required position. The bulb and stem having been made thoroughly dry, a small quantity of pure dry mercury is poured into the bulb at the lower end of the stem, and by means of an air-pump the pressure in the bulb is reduced to 20 or 25 centim. of mercury; in this way part of the air is removed from the thermometer, and on restoring the atmospheric pressure, mercury is driven up towards the top of the vertical part of the stem. If the thermometer is to be used for indicating temperatures near 500°, the quantity of air removed ought to be such that a difference of temperature of 1°, at ordinary atmospheric temperatures, makes a difference of about 1 mm. in the height of the mercury in the stem. The thermometer is graduated empirically by marking on the scale the points at which the mercury stands in the stem when the bulb is surrounded by *ice*, and by the vapours of *boiling water*, *boiling mercury*, and *boiling sulphur* respectively. These points being marked 0°, 100°, 350°, and 440°, the intermediate temperatures, as well as temperatures below 0° and above 440°, are supplied by inter- and extrapolation. It is evident that the four fixed points must be determined when the barometric pressure is sensibly constant. Berthelot does not admit greater variations than 1 mm. of mercury. When the instrument is used to indicate unknown temperatures, the barometric pressure will in general be different from that under which it was graduated; but the requisite adjustment can be made by immersing the bulb in pounded ice, and pushing the graduated scale up or down the stem until the zero-mark agrees with the extremity of the mercury-column.

The action of the apparatus is easily understood by reference to the laws of the expansion of air. With the dimensions of bulb and stem that have been indicated, the changes of volume of the air in the thermometer consequent on the mercury standing at different heights may be neglected without sensible error; hence, if H_0 be the pressure (measured in millimetres of mercury) which the air supports at 0°, and $H_0 + h$ the pressure supported by it at $t°$, we have the equation (comp. iii. 49)

$$H_0 + h = H_0(1 + at),$$

whence

$$1 + \frac{h}{H_0} = 1 + at,$$

or

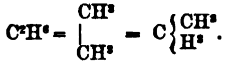
$$t = \frac{h}{H_0 a},$$

which shows that the temperature indicated is proportional to the depression h of the mercury-column from the position occupied by it when the thermometer is at 0°, since the denominator $H_0 a$ of the expression for t is constant. This calculation, however, is only approximate, as the expansion of the bulb, the expulsion of some air from the bulb into the stem, and the effect of variation of temperature in the part of the stem mass is then pulverised, and exhausted with water, and the clear solution is precipitated with common salt. The colouring matter thus obtained is purified by again dissolving and precipitating it (F. Laurent a. J. Castlehaz, *Repertory of Patent Inventions*, Oct. 1862, p. 339; *Dingl. pol. J.* clvi. 239).

ERYTHROCENTAURIN. $C^{27}H^{24}O^{8}$ (C. Mehu, *J. Pharm.* [4] iii. 265).—A substance allied to santonin, obtained from the common centaury (*Erythræa Centaurium*, Gentianaceæ). To prepare it, the aqueous extract of the flower-heads, or of the entire plant, is treated with 4 or 5 times its weight of alcohol; the syrupy residue of the alcoholic extract is repeatedly agitated with 4 vol. ether; and the ethereal solution is evaporated, whereby a yellowish-brown semifluid residue is obtained, which after a while yields crystals of impure erythrocentaurin. These, after being pressed and once recrystallised from water, are decolorised in ethereal solution by animal charcoal. On leaving the ether to evaporate, large colourless crystals are obtained, amounting to scarcely $\frac{1}{3}$ per thousand of the weight of the dried plant.

Pure erythrocentaurin is tasteless and inodorous, neutral and not hygroscopic, not volatile; melts at 136°, and solidifies again in the crystalline form. Its solution in chloroform neither acts on polarised light nor fluoresces. It dissolves in 1630 pts. water at 15°, in about 13·5 pts. at 100°, in 48 pts. of 86 p. c. alcohol at 15°, in 13·5 pts. chloroform, and 245 pts. ether; easily also in oils both fixed and volatile, in benzol, and in carbon bisulphide. Acids increase its solubility in water, but do not unite with it; from its colourless solution in strong sulphuric acid it is precipitated by water without alteration. It is not acted upon by nitric, hydrochloric, or chromic acid, bromine, iodine, or alkalis; when fused in chlorine gas, it is converted into a glutinous substance recrystallisable only from ether. Erythrocentaurin is decomposed by potassium permanganate, even at ordinary temperatures. When exposed to sunshine, it quickly acquires a bright red colour, but without alteration of weight or of its relations to solvents. This coloured erythrocentaurin yields colourless solutions which in the dark deposit colourless crystals. The red colour likewise disappears on heating the substance to about 130°. The coloration of erythrocentaurin (like that of santonin) is produced only by the most refrangible (blue or violet) rays of the spectrum; but santonin which has been turned yellow by light is not decolorised by heat.

ERYTHROGLUCIC ACID. Syn. with ERYTHRITIC ACID (p. 583).

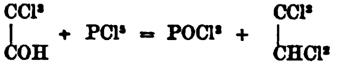


ETHANE. $C^{2}H^{6} = \begin{array}{l} CH^{3} \\ | \\ CH^{3} \end{array} = C\left\{\begin{array}{l} CH^{3} \\ H^{3} \end{array}\right.$. *Ethyl Hydride, Methyl, Dimethyl* (ii. 533; iii. 984).—This gas is evolved, together with carbon dioxide, by heating barium dioxide with acetic anhydride, barium acetate being produced at the same time (Schützenberger, *Bull. Soc. Chim.* [2] v. 278):

$$2(C^{2}H^{3}O)^{2}O + BaO^{2} = (C^{2}H^{3}O^{2})^{2}Ba + 2CO^{2} + C^{2}H^{6}.$$

Darling (*Chem. Soc. J.* [2] vi. 426) finds that this reaction is apt to give rise to violent explosion [arising from the formation of acetyl peroxide, i. 35], which, however, may be prevented by mixing the barium dioxide with dry sand. The gas then evolved consists, after removal of carbon dioxide, chiefly of methane (marsh gas) with a little carbon monoxide and about 17 p. c. ethane. Frankland's mode of preparation by heating methyl iodide with zinc, yields perfectly pure ethane; but is not well adapted for the preparation of large quantities. The best process is the electrolysis of potassium acetate. Darling's experiments fully confirm the results obtained by Schorlemmer (iii. 984) respecting the identity of the gas obtained by this process with that obtained from mercuric ethide. When treated with chlorine in diffused daylight, it is converted into a mixture of ethyl chloride, $C^{2}H^{5}Cl$, and chlorethyl chloride, $C^{2}H^{4}Cl^{2}$. The ethyl chloride thus obtained was converted into acetate, which by saponification with potash yielded pure ethyl alcohol.

Pentachlorethane. $C^{2}HCl^{5}$ (Paterno, *Compt. rend.* lxviii. 450).—Produced by the action of phosphorus pentachloride on anhydrous chloral:



$$\begin{array}{l} CCl^{3} \\ | \\ COH \end{array} + PCl^{5} = POCl^{3} + \begin{array}{l} CCl^{3} \\ | \\ CHCl^{2} \end{array}$$

A small quantity of the pentachloride is added to chloral contained in a retort fitted with an upright condenser; the mixture is warmed; another portion of pentachloride added as soon as the first action is over, the process being repeated till 1 mol. PCl^{5} has been added to 1 mol. chloral; and the reaction is completed by heating the mixture for some hours to the boiling point. Water is then added, *Table of Specific Heats of Elementary Substances.*

Name of Substance	Specific Heat	Authority
Aluminium	0·202	Kopp.
Antimony	·0495	Bunsen.
	·0523	Kopp.
Arsenic	·0822	Neumann (*Pogg. Ann.* cxxvi. 137).
„ (crystallised)	·0830	Bettendorff and Wüllner
„ (amorphous)	·0758	Ditto.
Bismuth	·0305	Kopp.
Boron (amorphous)	·254	—
„ (crystallised)	·230	—
Cadmium	·0542	—
„	·0548	Bunsen.
Calcium	·1670	—
Carbon (natural graphite)	·2019	Regnault (*Ann. Ch. Phys.* [4] vii. 450).
„ „ „ (purified)	·1977	Regnault.
„ „ „	·1955	Bettendorff and Wüllner.
„ „ „	·174	Kopp.
„ (gas carbon)	·1968	Regnault.
„ „ (purified)	·2000	—
„ „ „	·2040	Bettendorff and Wüllner.
„ „	·185	Kopp.
„ (iron graphite)	·1961	Bettendorff and Wüllner.
„ „	·166	Kopp.
„ (diamond)	·1483	Bettendorff and Wüllner.
Copper	·0930	Kopp.
Indium	·0570	Bunsen.
Iron	·112	—
Lead	·0315	—
Magnesium	·245	—
Ruthenium	·0611	—
Selenium (crystalline)	·08401	Bettendorff and Wüllner.
„ „	·0860	Neumann.
„ (amorphous)	·0953	Bettendorff and Wüllner.
Silicon (graphitoïdal)	·181	Kopp.
„ (crystalline)	·165	—
„ (fused)	·138	—
Silver	·0560	—
„	·0559	Bunsen.
Sulphur (rhombic)	·163 (between 17° and 45°)	Kopp.
„	·1712	Bunsen.
Tellurium	·0475	Kopp.
Tin	·0548	—
„ (cast)	·0559	Bunsen.
„ (allotropic)	·0545	—
Zinc	·0932	Kopp.
„	·0935	Bunsen.

Table of Specific Heats of Compounds.

Formula	Specific Heat	Authority	Formula	Specific Heat	Authority
Cu^2O	·111	Kopp.	$PbCO^3$	·0791	Kopp.
CuO	·128	—	$CaSiO^3$	·178	—
HgO	·0530	—	$Ca\frac{1}{2}Mg\frac{1}{2}SiO^3$	·186	—
PbO	·0553	—	$CuSiO^3.H^2O$	·182	—
MgH^2O^2	·312	—	$Mg\frac{11}{6}Fe\frac{1}{6}SiO^4$	·189	—
Fe^3O^4	·156	—		·189	—
$MgAl^2O^4$	·194	—	$Al^2K^2Si^6O^{16}$	·183	—
$Mg\frac{1}{2}Fe\frac{1}{2}Cr\frac{1}{2}Al\frac{1}{2}O^4$	·159	—	$Al^2Na^2Si^6O^{16}$	·190	—
Cr^2O^3	·177	—	$NaBO^2$	·2364	Neumann.
Fe^2O^3	·154	—	Na^2BO^7	·229	Kopp.
$Fe\frac{1}{2}Ti\frac{1}{2}O^3$	·177	—	$Na^2B^4O^7.10H^2O$	·385	—
$Mn^2O^3.H^2O$	·176	—	$PbMoO^4$	·0827	—
MnO^2	·159	—	$CaWO^4$	·0967	—
SiO^2	·186	—	$Fe\frac{1}{2}M\frac{1}{2}WO^4$	·0930	—
$Si\frac{1}{2}Zr\frac{1}{2}O^2$	·132	—	$PbCrO^4$	·0900	—
SnO^2	·0894	—	K^2CrO^4	·189	—
TiO^2	·157	—		·1840	Neumann.
TiO^2	·161	—	$K^2Cr^2O^7$	·186	Kopp.
MoO^3	·154?	—		·1857	Neumann.
WO^3	·0894?	—	$HKSO^4$	·244	Kopp.
Sb^2O^3	·0927	Neumann.	K^2SO^4	·196	—
B^2O^3	·2341	—		·1860	Neumann.
Cu^2S	·120	Kopp.	Na^2SO^4	·2293	Schüller.
$Cu\frac{1}{2}Fe\frac{1}{2}S$	·131	—		·227	Kopp.
HgS	·0517	—		·2280	Neumann.
PbS	·0490	—	$(NH^4)^2SO^4$	·350	Kopp.
ZnS	·120	—	$BaSO^4$	·108	—
FeS^2	·126	—	$CaSO^4$	·178	Kopp.
KCl	·171	—	$CuSO^4$	·184	Pape.
	·1663	Neumann.	$MgSO^4$	·225	—
$NaCl$	·213	Kopp.		·2165	Neumann.
	·219	—	$MnSO^4$	·182	Pape.
	·2070	Neumann.	$PbSO^4$	·0827	Kopp.
NH^4Cl	·373	Kopp.	$SrSO^4$	·135	—
	·3908	Neumann.	$ZnSO^4$	·174	Pape.
$AgCl$	·0894	—	$CuSO^4.H^2O$	·202	—
$RbCl$	·112	Kopp.	$MgSO^4.H^2O$	·264	—
$BaCl^2$	·0902	—	$ZnSO^4.H^2O$	·202	—
$HgCl^2$	·0640	—	$CaSO^4.2H^2O$	·259	Kopp.
$MgCl^2$	·191	—	$CuSO^4.2H^2O$	·212	Pape.
$PbCl^2$	·0692	Neumann.	$ZnSO^4.2H^2O$	·224	—
$BaCl^2.2H^2O$	·171	Kopp.	$FeSO^4.3H^2O$	·247	—
ZnK^2Cl^4	·152	—	$CuSO^4.5H^2O$	·285	Kopp.
PtK^2Cl^6	·113	—		·316	Pape.
SnK^2Cl^6	·133	—	$MnSO^4.5H^2O$	·323	Kopp.
Cr^2Cl^6	·143	—		·338	Pape.
NaI	·0881	Schüller.	$NiSO^4.6H^2O$	·313	Kopp.
$CaFl^2$	·209	Kopp.	$CoSO^4.7H^2O$	·343	—
$AlNa^3Fl^6$	·238	—	$FeSO^4.7H^2O$	·346	—
K^2CO^3	·206	—		·356	Pape.
	·2046	Neumann.	$MgSO^4.7H^2O$	·362	Kopp.
Na^2CO^3	·246	Kopp.		·407	Pape.
Rb^2CO^3	·123	—	$ZnSO^4.7H^2O$	·347	Kopp.
$CaCO^3$	·206	—		·328	Pape.
$CaCO^3$	·203	—	$NiSO^4.7H^2O$	·341	—
$CaMg\ C\ O^3$	·206	—	$K^2MgS^2O^8.6H^2O$	·264	Kopp.
Fe[illegible]Mn[illegible]Mg[illegible]CO^3	·166	—	$K^2NiS^2O^8.6H^2O$	·245	—

Table of Specific Heats of Compounds (continued).

Formula	Specific Heat	Authority	Formula	Specific Heat	Authority
$K^2ZnS^2O^8.6H^2O$	·270	Kopp.	C^2Cl^6 between 18° and 37°	·178	Kopp.
$Al\ K^2S^4O^{16}.24H^2O$	·371	—	C^2Cl^6 between 18° and 43°	·194	—
$Cr^2K^2S^4O^{16}.24H^2O$	·324	—	C^2Cl^6 between 18° and 50°	·277	—
$Na^2S^2O^3$ . .	·221	Pape.	$C^{10}H^8$ between −26° and 18°	·3096	Alluard.
$K^2S^4O^6$ . .	·197	—	$C^{10}H^8$ between 0° and 20°	·3208	—
BaS^2O^3 . .	·163	—	$C^{10}H^8$ between 20° and 65°	·3249	—
PbS^2O^3 . .	·092	—	$C^{10}H^{16}$	·4087	Neumann.
H^2KAsO^4 . .	·175	Kopp.	$C\ S^2$ (between 14° and 29·5°) . .	·2468	Schüller.
Ag^3PO^4 . .	·0896 ?	—	C^2H^6O . . .	·5748	Neumann.
H^2KPO^4 . .	·280	—	C^2H^6O between 17·5° and 20·5°	·6043	Dupré and Page.
$NaPO^3$ . .	·217	—	C^2H^6O between 16° and 30°	·6019	Schüller.
KNO^3 fused .	·227	—	$CHCl^3$ (between 16° and 35°) . .	·2337	—
KNO^3 crystallised	·232	—	$C^{12}H^{22}O^{11}$ crystallised .	·301	Kopp.
	·2343	Neumann.	$C^{12}H^{22}O^{11}$ amorphous .	·342	—
$NaNO^3$ fused .	·265	Schüller.	$C^6H^{14}O^6$ . . .	·324	—
$NaNO^3$ fused .	·256	Kopp.	$C^4H^6O^4$ . . .	·313	—
$NaNO^3$ crystallised	·257	—	$C^4H^6O^6$ . . .	·288	—
	·2747	Neumann.	$C^4H^6O^6.H^2O$ . .	·319	—
NH^4NO^3 . .	·455	Kopp.	$C^2H^2BaO^4$ . . .	·143	—
BaN^2O^6 .	·145	—	$C^2K^2O^4.H^2O$ . .	·236	—
	·1402	Neumann.	$C^4H^3KO^4.2H^2O$ . .	·283	—
PbN^2O^6 .	·110	Kopp.	$C^4H^5KO^6$ . . .	·257	—
	·1173	Neumann.	$C^4H^4NaKO^6.4H^2O$.	·328	—
SrN^2O^6 . .	·181	Kopp.	$C^8H^{10}CaO^{10}.8H^2O$.	·338	—
$AgNO^3$ . .	·1395	Neumann.			
$KClO^3$ . .	·194	Kopp.			
$BaCl^2O^6$ . .	·157	—			
$KClO^4$ . .	·190	—			
$KMnO^4$ . .	·179	—			
HgC^2N^2 . .	·100	—			
$ZnK^2C^4N^4$.	·241	—			
$FeK^3C^6N^6$ . .	·233	—			
$FeK^4C^6N^6.3H^2O$	·280	—			

The specific heats of alcohol and benzene at different temperatures have been determined by Schüller (*Pogg. Ann., Ergänzungsbd.* v. 116). For the mean specific heats of these liquids between 0° and any other temperature $t°$, his experiments lead to the following results:

Alcohol . . .	$0·5585 + 0·00093195t + 0·0000008463t^2$.
Benzene . . .	$0·3798 + 0·00072t$.

Values having reference to much higher temperatures have been given by Hirn (*Ann. Ch. Phys.* [4] x. 63) for alcohol, ether, sulphide of carbon, bichloride of carbon, and oil of turpentine.

The specific heat of various aqueous solutions has been investigated by Schüller (*Pogg. Ann.* cxxxvi. 70 and 235) and Thomsen (*Zeitschr. f. Chem.* 1870, p. 729); the following tables give the principal results:

Specific Heat of Aqueous Solutions (Schüller).

Salt in 100 parts of Water	Sodium Chloride	Potassium Chloride	Ammonium Chloride	Sodium Sulphate	Sodium Iodide	Sodium Nitrate	Potassium Nitrate
4	—	·9558	—	—	—	—	—
5	·9306	—	—	—	—	—	—
8	—	·9140	—	—	—	—	—
10	·8909	—	·9100	·9253	·9135	·9320	·9182
12	—	·8876	—	—	—	—	—
15	·8606	—	—	·8959	—	—	—
16	—	·8503	—	—	—	—	—
20	·8304	·8195	·8403	·8704	·8408	·8768	·8589
24	—	·7935	—	—	—	—	—
25	·8479	—	—	·8523	—	—	—
28	—	·7680	—	—	—	—	—
30	·7897	—	·7946	·8320	·7811	·8341	·8090
32	—	·7476	—	—	—	—	—
33·6	·7752	—	—	—	—	—	—
35	·7713	—	—	—	—	—	—
37	—	—	·7644	—	—	—	—
40	—	—	—	·8074	·7343	·7998	—
50	—	—	—	—	—	·7673	—

Specific Heat of Aqueous Acids and Alkalis (Thomsen).

a	Sulphuric Acid $SO^3 + aH^2O$	Nitric Acid $HNO^3 + aH^2O$	Hydrochloric Acid $HCl + aH^2O$	Tartaric Acid $C^4H^6O^6 + aH^2O$	Potash $HKO + aH^2O$	Soda $HNaO + aH^2O$	Ammonia $HNH^4O + aH^2O$	a
5	·545	—	—	—	—	·846	—	7·5
10	·700	·767	·748	·745	—	·878	—	15
20	·820	·848	·854	·831	·876	·919	·9965	30
50	·918	·929	·931	·910	·915	·942	·9975	50
100	·955	·962	·963	·951	·954	·967	·9984	100
200	·976	·981	·978	·974	·974	·982	—	200

If, when a salt is dissolved in water, both the water and the salt retain the same specific heat that they possess when separate, the specific heat C_p of a solution containing p parts of the salt in 100 parts of water would be represented by the formula

$$C_p = \frac{100 + pk}{100 + p},$$

where k is the specific heat of the salt in the separate state. It appears, however, from Schüller's experiments that, in the cases investigated by him, the relation between the specific heat of a solution and the specific heats of its constituents is less simple than that expressed by this formula. He finds that the specific heat of a solution may be represented by

$$C_p = r\,\frac{100 + pk}{100 + p},$$

where r is a coefficient (in the cases examined always less than unity) which may either be sensibly constant[*] or, as is more commonly the case, may vary with the strength of the solution. Hence, in order to calculate the specific heat of a solution of given strength, we require to know the values of r and k, which correspond to the salts employed. Schüller deduces from his experiments the values of r given in the next table; the values of k are in some cases those resulting from his own experiments, and in others they are taken from Regnault's or Kopp's determinations:

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[*] It is clear that, as the proportion of salt diminishes, the specific heat of a solution must approach indefinitely near to unity: hence, as Thomsen points out, the above formula with $r = const.$ is inapplicable to very dilute solutions.

Name of Salt	k	r
Potassium Chloride . .	·1729	$1 - 0·003194p + 0·000036p^2$
Sodium Chloride . . .	·214	$0·9624$
Ammonium Chloride . .	·373	$1 - 0·003996p + 0·0000497p^2$
Sodium Sulphate . . .	·2291	$1 - 0·00096p + 0·000046p^2$
Sodium Iodide . . .	·0881	$0·9925$
Sodium Nitrate . . .	·2671	$1 - 0·00025p + 0·000012p^2$
Potassium Nitrate . .	·2387	$0·98905 - 0·000255p$

The specific heat of mixtures of *alcohol* and water in various proportions has been examined by Dupré and Page (*Phil. Trans.* 1869, p. 591); the following table gives an epitome of their results:

Specific Heat of Aqueous Alcohol.

Percentage of Absolute Alcohol by Weight	Specific Heat	Percentage of Absolute Alcohol by Weight	Specific Heat
5	1·0150	50	·9063
10	1·0358	60	·8433
20	1·0436	70	·7844
30	0·0260	80	·7169
40	0·9681	90	·6574
45	0·9419	100	·6043

The most remarkable result of this investigation is that when alcohol is added to water, the specific heat of the mixture increases until the proportion by weight of alcohol amounts to 20 per cent., when the specific heat has the maximum value 1·0436; beyond this point, it diminishes as more alcohol is added, until, with a mixture containing nearly 35 per cent. of alcohol, the specific heat is equal to that of pure water. Closely accordant results have been obtained by Schüller (*Pogg. Ann.*, *Ergänzungsbd.* v. 116, 192), who has also determined the specific heats of various mixtures of alcohol, sulphide of carbon, chloroform, and benzene.

Comparison of the Specific Heats of Gases under Constant Pressure and Constant Volume (iii. 40).—The following table gives the values found by various experimenters for the ratio of the specific heat of air under constant pressure to its specific heat when kept at a constant volume:

Ratio	Experimenter
1·4196	Masson (*Ann. Ch. Phys.* [3] liii. 269).
1·4025	Weisbach (quoted by Zeuner, *Wärmetheorie*, 1860, p. 38).
1·41	Cazin (*Ann. Ch. Phys.* [3] lxvi. 243).
1·3845	Hirn (*Théorie mécaniq. de la Chaleur*, 1865, p. 69).
1·302	Kohlrausch (*Pogg. Ann.* cxxxvi. 618).
1·41	Jamin and Richard (*Compt. rend.* lxxi. 336).

All these results, except the last, are deduced from observations of the change of temperature which a mass of air undergoes when it is subjected to a sudden change of density, work being at the same time done either by it or upon it. Jamin and Richard compared the rise of temperature produced by a given quantity of heat (generated by an electric current traversing a metallic wire) in a quantity of air allowed to expand under constant pressure, with the rise of temperature caused in air which was not allowed to expand.

The values given for the corresponding ratio in the case of some other gases are as follows:

Name of Gas	Ratio of Specific Heat	Experimenter
Oxygen	1·41	Cazin (loc. cit.).
Nitrogen	1·41	—
Hydrogen . . .	1·41	—
	1·376	Masson (quoted by Cazin).
	1·41	Jamin and Richard (loc. cit.).
Carbonic oxide . .	1·41	Cazin.
Ammonia . . .	1·328	—
Carbonic acid . . .	1·291	—
	1·30	Masson.
	1·29	Jamin and Richard.
Nitrous oxide . . .	1·285	Cazin.
Sulphurous acid . .	1·262	—
Marsh gas . . .	1·257	—
Ether vapour . . .	1·079	—

Expansion by Heat. *General Formulæ relating to Expansion.*—If the volume of a given body at 0° be represented by V_0, and the volume of the same body at $t°$ by V, the increase of bulk between 0° and $t°$, expressed as a fraction of the volume at 0°, will be represented by

$$\frac{V - V_0}{V_0} = e:$$

this quantity may be conveniently called the *expansion of the body between 0° and t°*. Similarly, if the volume at any other temperature $t'°$ be denoted by V', the expansion between 0° and $t'°$ will be represented by

$$\frac{V' - V_0}{V_0} = e'.$$

These formulæ give the following for the relations between V_0, V, and V':

$$V = V_0(1 + e) \qquad V' = V_0(1 + e') \qquad V' = V\frac{1 + e'}{1 + e}.$$

The last of these expressions may be written in a simpler form; for if e be small compared with unity (as it always is in reality), the value of the fraction will not be sensibly changed if we subtract e from both numerator and denominator: this gives:

$$V' = V(1 + e' - e) \text{ nearly.}$$

If we divide the expansion between 0° and any other temperature $t°$ by the number of degrees within which it takes place, the quotient is the *average expansion, or average increase of bulk of unit volume, between 0° and the temperature in question.* This quantity is called the *mean coefficient of expansion* between 0° and $t°$. Thus if Δ and Δ' are the mean coefficients of expansion between 0° and the temperatures $t°$ and $t'°$ respectively, we have

$$\Delta = \frac{e}{t} = \frac{V - V_0}{V_0 t}, \text{ and } \Delta' = \frac{e'}{t'} = \frac{V' - V_0}{V_0 t'}.$$

In general, the values of Δ and Δ' are not equal except for the permanent gases, but if the temperatures $t°$ and $t'°$ lie near together, their difference may be neglected. Within limits where this is allowable, the relations between the volumes at 0°, $t°$, and $t'°$ may be written

$$V = V_0(1 + \Delta t) \qquad V' = V_0(1 + \Delta t')$$

$$V' = V\frac{1 + \Delta t'}{1 + \Delta t} = V[1 + \Delta(t' - t)] \text{ nearly.}$$

The fraction of its volume at 0° by which a given mass of any substance would expand when heated from the temperature $t°$ to the temperature $(t + 1)°$, if it continued to expand at a constant rate for one degree, is called the *coefficient of expansion at t°*. It is the limit towards which the value of the expression $\frac{V' - V}{V_0(t' - t)}$, or $\frac{e' - e}{t' - t}$, approaches as the interval of temperature $t' - t$ gets smaller and smaller.

Expansion of Mercury.—If the mean coefficient of expansion of mercury between 0° and a series of other temperatures, differing from each other by a constant amount, be calculated from the numbers resulting from Regnault's experiments (iii. 55, 56), the value obtained is found to increase uniformly as the temperature for which it is calculated rises. Hence, if a be the value of the mean coefficient of expansion between 0° and 1°, and b be the increment in the value of the mean coefficient corresponding to a rise of one degree in the higher limit of the interval for which it is calculated, we may write as general expressions for the mean coefficients of expansion between 0° and any other temperatures $t°$ and $t'°$

$$\Delta = a + bt \text{ and } \Delta' = a + bt'.$$

The values of a and b may be found by introducing into the general formula the values of Δ given by experiment for any two values of t, and then solving the two resulting equations for a and b successively. The values calculated by Regnault, from a discussion of all his experiments, are

$$a = 0{\cdot}000179006 \text{ and } b = 0{\cdot}0000000252316.$$

Expressing the expansion of mercury between 0° and any two temperatures $t°$ and $t'°$ in terms of these constants, we have

$$e = \Delta t = at + bt^2 \text{ and } e' = \Delta t' = at' + bt'^2;$$

consequently for the mean coefficient of expansion between $t°$ and $t'°$, we get

$$\Delta_{t'-t} = \frac{e' - e}{t' - t} = a + b(t' + t).$$

But if the temperatures $t'°$ and $t°$ are indefinitely near to each other, we have $t' + t = 2t$, and hence the coefficient of expansion of mercury *at* $t°$ is expressed by

$$\Delta_t = a + 2bt = 0{\cdot}000179006 + 0{\cdot}0000000504632t.$$

The mean coefficient of expansion of mercury between 0° and 100° has been redetermined by Matthiessen (*Phil. Trans.* 1866, p. 244), by weighing mercury in water at various temperatures. His experiments give the value

0·0001812.

Expansion of Water (iii. 52).—The rate of expansion of *water* by heat has been investigated by Matthiessen (*Phil. Trans.* 1866, p. 231) and by Rossetti (*Ann. Ch. Phys.* [4] x. 461; xvii. 370). The method employed by Matthiessen was to determine first the coefficient of linear expansion of glass,* by direct measurement upon a long glass rod, to calculate the coefficient of cubical expansion of the glass by multiplying the linear coefficient by 3, and finally to determine the weight of a piece of the same glass in water at various temperatures. Rossetti's method consisted in ascertaining the weight of water which occupied a known volume at various temperatures, the volume being found by observing the height at which the water stood in a graduated capillary stem connected with a large bulb like that of a thermometer, the capacity of the bulb and of each division of the stem, as well as the coefficient of expansion, having been previously found (apparently by weighings of the instrument when filled to different points with mercury at known temperatures). These determinations therefore depend upon Regnault's measurement of the coefficient of expansion of mercury; Matthiessen's experiments, on the other hand, are of importance as being the only accurate series of observations made by a method which does not presuppose a knowledge of the expansion of mercury. The following table gives the density and volume of water for each degree between −10° and 100°, as calculated by Rossetti from his own experiments and those of Kopp, Pierre, Despretz, Hagen, Matthiessen, Weidner (*Pogg. Ann.* cxxix. 300; *Jahresb.* 1866, p. 100), and Kremers. The columns headed d_t and v_t give the density and volume at $t°$ compared with the density and volume at 0° taken as unity; in the columns headed D_t and V_t the comparison is with the density and volume at 4°. Two columns are added giving a few of the special values found by Weidner, Matthiessen, and Rossetti.

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* The approximate composition of the mixture from which the glass was made was '3 parts sand, 2 lead, and 1 alkali.' The mean coefficient of linear expansion was found = 0·00000729.

Expansion of Water.

t	d_t	v_t	D_t	V_t	V_t Weidner	V_t Rossetti
−10°	0·998274	1·001729	0·998145	1·001858	1·001904	
− 9	·998556	1·001449	·998427	1·001575		
− 8	·998814	1·001191	·998685	1·001317		
− 7	·999040	1·000963	·998911	1·001089		
− 6	·999247	1·000756	·999118	1·000883		
− 5	·999428	1·000573	·999298	1·000702	1·000710	
− 4	·999584	1·000416	·999455	1·000545		1·000516
− 3	·999719	1·000281	·999590	1·000410		
− 2	·999832	1·000168	·999703	1·000297		
− 1	·999926	1·000074	·999797	1·000208		
0	1·000000	1·000000	·999871	1·000129	1·000137	1·000135
+ 1	1·000057	0·999943	·999928	1·000072		
2	1·000098	·999902	·999969	1·000031		
3	1·000120	·999880	·999991	1·000009		
4	1·000129	·999871	1·000000	1·000000	1·000000	1·000000
					Matthiessen	
5	1·000119	·999881	0·999990	1·000010	1·000006	1·000006
6	1·000099	·999901	·999970	1·000030		
7	1·000062	·999938	·999933	1·000067		
8	1·000015	·999985	·999886	1·000114		
9	0·999953	1·000047	·999824	1·000176		
10	·999876	1·000124	·999747	1·000253	1·000271	1·000248
11	·999784	1·000216	·999655	1·000345		
12	·999678	1·000322	·999549	1·000451		
13	·999559	1·000441	·999430	1·000570		
14	·999429	1·000572	·999299	1·000701		
15	·999289	1·000712	·999160	1·000841	1·000892	
16	·999131	1·000870	·999002	1·000999		1·000991
17	·998970	1·001031	·998841	1·001160		
18	·998782	1·001219	·998654	1·001348		
19	·998588	1·001413	·998460	1·001542		
20	·998388	1·001615	·998259	1·001744	1·001814	1·001746
21	·998176	1·001828	·998047	1·001957		
22	·997953	1·002049	·997826	1·002177		
23	·997730	1·002276	·997601	1·002405		
24	·997495	1·002511	·997367	1·002641		
25	·997249	1·002759	·997120	1·002888		
26	·996994	1·003014	·996866	1·003144		
27	·996732	1·003278	·996603	1·003408		
28	·996460	1·003553	·996331	1·003682		
29	·996179	1·003835	·996051	1·003965		
30	·995894	1·004123	·995765	1·004253	1·004345	
31	·99560	1·00442	·99547	1·00455		
32	·99530	1·00473	·99517	1·00486		1·00488
33	·99498	1·00505	·99485	1·00518		
34	·99465	1·00538	·99452	1·00551		
35	·99431	1·00572	·99418	1·00586		
36	·99396	1·00608	·99383	1·00621		
37	·99360	1·00645	·99347	1·00657		
38	·99323	1·00682	·99310	1·00694		
39	·99286	1·00719	·99273	1·00732		
40	·99248	1·00757	·99235	1·00770	1·00773	1·00771

Expansion of Water (continued).

t	d_t	v_t	D_t	V_t	V_t Matthiessen	V_t Rossetti
+41	0·99210	1·00796	0·99197	1·00809		
42	·99171	1·00836	·99158	1·00849		
43	·99131	1·00876	·99118	1·00889		
44	·99091	1·00917	·99078	1·00929		
45	·99050	1·00958	·99037	1·00971		
46	·99009	1·01001	·98996	1·01014		
47	·98967	1·01044	·98954	1·01057		
48	·98923	1·01088	·98910	1·01101		
49	·98878	1·01134	·98865	1·01148		
50	·98833	1·01181	·98820	1·01195	1·01197	1·01187
51	·98787	1·01229	·98773	1·01243		
52	·98741	1·01278	·98725	1·01292		
53	·98694	1·01327	·98677	1·01341		
54	·98646	1·01376	·98629	1·01390		
55	·98598	1·01425	·98582	1·01439		
56	·98550	1·01474	·98535	1·01488		
57	·98501	1·01524	·98487	1·01537		
58	·98450	1·01574	·98438	1·01587		
59	·98401	1·01625	·98388	1·01638		
60	·98351	1·01677	·98338	1·01691	1·01696	1·01686
61	·98299	1·01731	·98286	1·01744		
62	·98247	1·01785	·98234	1·01798		
63	·98194	1·01839	·98182	1·01852		
64	·98140	1·01895	·98128	1·01908		
65	·98086	1·01951	·98074	1·01964		
66	·98031	1·02008	·98019	1·02021		
67	·97977	1·02065	·97964	1·02078		
68	·97921	1·02124	·97908	1·02137		
69	·97864	1·02183	·97851	1·02196		
70	·97807	1·02243	·97794	1·02256	1·02265	1·02253
71	·97749	1·02303	·97736	1·02316		
72	·97690	1·02365	·97677	1·02378		
73	·97631	1·02427	·97618	1·02440		
74	·97571	1·02490	·97558	1·02503		
75	·97511	1·02553	·97498	1·02566		
76	·97450	1·02617	·97438	1·02630		
77	·97389	1·02681	·97377	1·02694		
78	·97328	1·02745	·97316	1·02758		
79	·97267	1·02809	·97255	1·02822		
80	·97206	1·02874	·97194	1·02887	1·02953	1·02884
81	·97145	1·02939	·97132	1·02952		
82	·97083	1·03005	·97070	1·03018		
83	·97020	1·03072	·97007	1·03085		
84	·96956	1·03139	·96943	1·03153		
85	·96892	1·03207	·96879	1·03221		
86	·96828	1·03276	·96815	1·03289		
87	·96764	1·03345	·96751	1·03358		
88	·96699	1·03414	·96687	1·03427		
89	·96634	1·03484	·96622	1·03497		
90	·96568	1·03554	·96556	1·03567	1·03581	1·03566
91	·96502	1·03625	·96490	1·03638		
92	·96435	1·03697	·96423	1·03710		
93	·96368	1·03770	·96356	1·03782		

Expansion of Water (continued).

t	d_t	v_t	D_t	V_t	V_t Matthiessen	V_t Rossetti
+94	0·96300	1·03844	0·96288	1·03856		
95	·96231	1·03918	·96219	1·03931		
96	·96161	1·03993	·96149	1·04006		
97	·96091	1·04069	·96079	1·04082		
98	·96020	1·04145	·96008	1·04158		
99	·95949	1·04222	·95937	1·04235		
100	·95878	1·04300	·95865	1·04312	1·04316	1·04312

The numbers in the above table show that the expansion-curve for water is not symmetrical on the two sides of the point of greatest density, but that the expansion caused by a given fall of temperature from that point is perceptibly greater than that caused by an equal rise of temperature.

The following table gives the temperature at which solutions of chloride of sodium of various strengths possess the greatest density, as well as the densities of the solutions at these temperatures, and their freezing points, as determined by Rossetti (*loc. cit.*):

Maximum Density of Solutions of Salt.

Chloride of Sodium in 100 parts of water. p	Density at 0°. o	Density at maximum. d_T	Temperature of maximum density. T	Depression of temperature of maximum density. A	Depression of freezing point. C	$\frac{A}{p}$	$\frac{C}{p}$
			°	°	°		
0	1·000000	1·000130	+ 4·00	0·00	0·00	—	—
0·5	1·003925	1·003988	+ 3·00	1·00	0·32	2·00	0·64
1	1·007634	1·007666	+ 1·77	2·23	0·65	2·23	·65
2	1·015366	1·015367	− 0·58	4·58	1·27	2·29	·63
3	1·023530	1·023583	− 3·24	7·24	1·90	2·41	·63
4	1·030669	1·030890	− 5·63	9·63	2·60	2·41	·65
6	1·045975	1·046952	− 11·07	15·07	3·91	2·51	·65
7		—	− 13·69	17·69	4·60	2·53	·65
8		1·063102	− 16·62	20·62	5·12	2·58	·64
Water of the Adriatic collected in June	1·026699	1·026774	− 3·21	7·21	1·90		
Water of the Adriatic collected in November	1·028141	1·028261	− 3·90	7·90	2·10		

These results show that (up to a concentration of 8 parts in 100) the depression of the freezing point caused by the solution of common salt in water is strictly proportional to the quantity of salt present, but that the depression of the point of maximum density increases rather more rapidly than the quantity of salt. In these respects Rossetti's experiments entirely confirm the earlier experiments of Depretz (iii. 60) and Rüdorff (iii. 80).

Expansion of other Liquids.—The expansion of water and of several other liquids at temperatures above their usual boiling points has been examined by Hirn (*Ann. Ch. Phys.* [4] x. 32); his results lead to the numbers given in the next table:

Expansion of Liquids at High Temperatures.

t	Water	Alcohol	Sulphide of Carbon	Bichloride of Carbon	Oil of Turpentine
0	—	1·00000	1·00000	1·00000	1·00000
30	—	—	—	1·03489	—
40	—	—	1·04946	—	1·03401
50	—	1·05429	—	—	—
70	—	—	—	1·08909	—
80	—	—	1·10608	—	1·07667
100	1·04315	1·12735	—	—	—
110	—	—	—	1·15310	—
120	1·05992	—	1·17515	—	1·12453
140	1·07949	—	—	—	—
150	—	1·24074	—	1·23296	—
160	1·10149	—	1·26572	—	1·17836
180	1·12678	—	—	—	—
200	1·15900	1·47665	—	—	—

The limits of temperature employed in the experiments from which the above values were deduced were—for *water*, 101°·7 and 181°·95; for *alcohol*, 19°·09 and 151°·3; for *sulphide of carbon*, 22°·39 and 145°·66; for *chloride of carbon*, 31°·29 and 140°·67; for *oil of turpentine*, 17·99° and 161·45°. In the case of water, the volume at 100° was assumed to be 1·04315 as compared with that at 4° taken as unity, on the authority of Depretz's experiments.

Experiments on the expansion of benzene and some of its homologues have been made by Louguinine (*Ann. Ch. Phys.* [4] xi. 453), for the results of which see pp. 278, 279.

Expansion of Solids.—The expansion of a considerable number of carefully purified metals and alloys has been determined by Matthiessen (*Phil. Trans.* 1866, p. 861; *Pogg. Ann.* cxxx. 50; abstract in *Proc. Roy. Soc.* xv. 220), by weighing the substances under examination in water at various temperatures. His principal results are given in the table on the following page, where the numbers given in the columns headed a and b respectively are the values of the coefficients which enter into the formula

$$V_t = V_0 (1 + at + bt^2),$$

expressing the relation between the volume at the temperature t° and the volume at 0°. The method of experiment adopted by Matthiessen did not admit of his employing higher temperatures than 100°: hence this temperature marks the limit up to which the above numbers may be taken as expressing the results of actual observation. It results from these measurements that the expansion of an alloy is sensibly equal to the sum of the expansions of its constituents, each multiplied by the fraction which represents the proportion by volume in which it enters into the composition of the alloy.

The expansion of a great number of crystallised substances has been examined by Fizeau (*Ann. Ch. Phys.* [4] viii. 335; *Pogg. Ann.* cxxviii. 564; *Compt. rend.* lxii. 1101, 1133; lxiv. 314, 771; *Pogg. Ann.* cxxxii. 292; *Compt. rend.* lxvi. 1005, 1072; *Pogg. Ann.* cxxxv. 372; *Compt. rend.* lxviii. 1125; *Pogg. Ann.* cxxxviii. 26), by a method depending upon the accuracy with which extremely minute movements can be appreciated by observing the changes they produce in a system of 'Newton's rings.' He found, as a general result, that the coefficient of expansion of the substances examined by him is not constant, but is greater at high than at low temperatures; the rate of change of the coefficient with change of temperature, however, he found to be constant. Hence if α be the mean coefficient of expansion for the interval of temperature t° to $t^{\circ\prime}$, α_1 the mean coefficient for the interval $t_1{}^\circ$ to $t_1{}'$, and $\theta = \dfrac{t + t'}{2}$ and $\theta_1 = \dfrac{t_1 + t_1{}'}{2}$ respectively the mean temperatures of the two intervals, the ratio of the difference of the two coefficients to the difference of the two mean temperatures, namely

$$\frac{\alpha - \alpha_1}{\theta - \theta_1} = \frac{\Delta\alpha}{\Delta\theta},$$

has a constant value for the same substance. Further, if α_1 be the coefficient for any interval of which the mean temperature is θ°, the coefficient a_τ for an interval the mean temperature of which is $\tau^\circ = (\theta \pm n)^\circ$ will be given by the formula

$$a_\tau = a_\theta \pm n\frac{\Delta a}{\Delta\theta}.$$

Hence the expansion of any substance can be expressed completely by means of the two constants a_θ and $\frac{\Delta a}{\Delta\theta}$, and it is the values of these constants that are given in the following tables of Fizeau's results. The relation between the formulæ of expansion expressed by means of these coefficients and those commonly employed will be understood clearly by noticing that the length at t'° of a body which measures l_t at t° is given by the formula

$$l_{t'} = l_t[1 + a_\tau(t' - t)] = l_t\left[1 + \left(a_\theta \pm n\frac{\Delta a}{\Delta\theta}\right)(t' - t)\right],$$

where τ is the mean temperature of the interval $t' - t$, and n the number of degrees by which it differs from θ, the temperature for which the value of a is given in the tables; and by observing further that the values of the coefficients in the ordinary formula $l_t = l_0(1 + at + bt^2)$ are given by the equations $a = a_0$ and $2b = \frac{\Delta a}{\Delta\theta}$.

Expansion of Metals and Alloys (Matthiessen).

Name of Substance		a	b	Vol. at 100°, the vol. at 0° being = 1
Pure Metals.				
Cadmium		$10^{-4} \times 0·8078$	$10^{-6} \times 0·140$	1·009478
Zinc		— × 0·8222	— × 0·0706	1·008928
Lead		— × 0·8177	— × 0·0222	1·008399
Tin		— × 0·6100	— × 0·0789	1·006889
Silver		— × 0·5426	— × 0·0405	1·005831
Copper		— × 0·4443	— × 0·0555	1·004998
Gold		— × 0·4075	— × 0·0336	1·004411
Bismuth		— × 0·3502	— × 0·0446	1·003948
Palladium		— × 0·3032	— × 0·0280	1·003312
Antimony		— × 0·2770	— × 0·0397	1·003167
Platinum		— × 0·2534	— × 0·0104	1·002658
Alloys, containing per cent. by volume:				
Sn^4 Pb	22·28Pb	$10^{-4} \times 0·6200$	$10^{-6} \times 0·0988$	1·007188
Sn Pb^4	82·09Pb	— × 0·8087	— × 0·0332	1·008419
Cd Pb	58·49Pb	— × 0·9005	— × 0·0133	1·009138
Sn^4 Zn	87·46Sn	— × 0·6377	— × 0·0807	1·007184
Sn^6 Zn	91·28Sn	— × 0·6236	— × 0·0822	1·007058
Bi^{44} Sn	0·85Sn	— × 0·3793	— × 0·0271	1·004064
Bi Sn^2	42·81Sn	— × 0·4997	— × 0·0101	1·005098
Bi^{24} Pb	1·76Pb	— × 0·3868	— × 0·0218	1·004086
Bi Pb^2	46·26Pb	— × 0·8462	— × 0·0159	1·008621
Au Sn^2	60·85Sn	— × 0·3944	— × 0·0289	1·004233
Au^2 Sn^7	73·14Sn	— × 0·4165	— × 0·0263	1·004428
Ag^4 Au	19·86Au	— × 0·5166		1·005166
Ag Au	49·79Au	— × 0·4916		1·004916
Ag Au^4	79·86Au	— × 0·3115	— × 0·1185	1·004300
Copper-zinc (71 p. c. copper)	by weight	— × 0·5161	— × 0·0558	1·005719
Silver-platinum (66·6 p. c. silver)		— × 0·4246	— × 0·0322	1·004568
Silver-copper (36·1 p. c. silver)		— × 0·4884	— × 0·0552	1·005436
Silver-copper (71·6 p. c. silver)		— × 0·4413	— × 0·0130	1·005713
Gold-copper (66·6 p. c. gold)		— × 0·4015	— × 0·0642	1·004657

In the majority of solid substances, the linear expansion which takes place in consequence of a given change of temperature is not the same in different directions, so that an indefinite number of different values might be found for the coefficient of expansion of the same substance, by measuring it in as many different directions. These different rates of expansion may however in all cases be referred to *three* principal rates of expansion in three directions at right angles to each other, so that the expansion in any given direction may be regarded as the resultant expansion due to three independent components, each of which takes part in the resultant expansion to an extent proportional to the length of the projection upon its own direction of a line parallel to the direction of the resultant expansion. Hence if α, α', and α'' are the three primary coefficients of expansion, the coefficient of expansion in any direction making the angles δ, δ', and δ'' respectively with the directions of the three primary directions of expansion may be represented by

$$D = \alpha \cos^2 \delta + \alpha' \cos^2 \delta' + \alpha'' \cos^2 \delta'' \quad . \quad . \quad . \quad (1).$$

But, since the angles δ, δ', and δ'' are the angles made by the same straight line with three axes at right angles to each other, they fulfil the relation

$$\cos^2 \delta + \cos^2 \delta' + \cos^2 \delta'' = 1 \quad . \quad . \quad . \quad . \quad (2).$$

In the case of *amorphous* substances, and those which crystallise in forms belonging to the *cubical* system, the three coefficients of expansion are equal, or $\alpha = \alpha' = \alpha''$: hence formula (1) becomes $D = \alpha(\cos^2 \delta + \cos^2 \delta' + \cos^2 \delta'') = \alpha$. That is to say, the expansion of such substances is the same in all directions.

In crystallised substances belonging to the *quadratic* and *hexagonal* systems, the coefficient of expansion has a special value corresponding to the direction of the principal crystallographic axis, but the coefficients for all directions equally inclined to the principal axis are the same. Hence the expansion of such crystals can be represented by making $\alpha' = \alpha''$ in formula (1), which then becomes $D = \alpha \cos^2 \delta + \alpha'(\cos^2 \delta' + \cos^2 \delta'')$; or, since by formula (2) $\cos^2 \delta' + \cos^2 \delta'' = 1 - \cos^2 \delta = \sin^2 \delta$, the expansion may be expressed by $D = \alpha \cos^2 \delta + \alpha' \sin^2 \delta$. For all directions perpendicular to the axis, $\delta = 90°$, and consequently $\cos \delta = 0$, and $\sin \delta = 1$; hence for all such directions $D = \alpha'$.

In crystals belonging to the *right prismatic system* the three principal axes of expansion are parallel to the crystallographic axes, but the coefficients of expansion corresponding to them are all unequal. The expansion of *monoclinic* crystals corresponds also to three unequal coefficients in directions at right angles to each other, but the relation between the positions of the crystallographic axes and those of the axes of expansion cannot be stated in general terms.

In all cases the coefficient of *cubical* expansion is equal to the sum of the three coefficients of linear expansion, or

$$\alpha_c = \alpha' + \alpha + \alpha'' \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

a relation which becomes $\alpha_c = 3\alpha$ when applied to amorphous substances or to crystals belonging to the regular system, and becomes $\alpha_c = \alpha + 2\alpha'$ when applied to substances crystallised in forms belonging to the quadratic or hexagonal systems. In all cases also the coefficient of *mean linear* expansion is given by the expression

$$\alpha_m = \tfrac{1}{3}(\alpha + \alpha' + \alpha'') = \tfrac{1}{3}\alpha_c.$$

The mean linear or the cubical expansion may thus be deduced from the measurement of one, two, or three coefficients of linear expansion, according to the crystalline system to which the substance belongs. It may however be obtained from a single measurement of the coefficient of expansion in a direction equally inclined to the three axes of expansion; for if in equation (1) we make $\delta = \delta' = \delta''$, we get $D = (\alpha + \alpha' + \alpha'') \cos^2 \delta$. But, under these conditions, equation (2) gives $\cos^2 \delta = \tfrac{1}{3}$, or $\delta = 54° 44'$, and therefore $D = \tfrac{1}{3}(\alpha + \alpha' + \alpha'') = \alpha_m$.

In the following tables of results, the letters A, B, and C denote the coefficients of expansion parallel to the three principal axes of expansion respectively, M denotes the coefficient of mean linear expansion obtained by direct measurement in a direction inclined at 54° 44′ to the axes, and M_1 the same coefficient calculated by the formula $\alpha_m = \tfrac{1}{3}(\alpha + \alpha' + \alpha'')$, or when two coefficients are equal, $\alpha_m = \tfrac{1}{3}(\alpha + 2\alpha')$. The numbers in the first table are given chiefly by way of illustration of the above-mentioned relations between expansion and crystalline form:

Expansion of Crystals.

	α_{40}
Fluor spar (cubic):	
1. At right angles to an octohedral cleavage face . . .	·00001911 ·00001910
2. At right angles to the cubical face of another crystal . . .	·00001910
3. At right angles to a face cut at 5° to the face of a cube (another crystal) . . .	·00001915
Galena (cubic):	
1. At right angles to a cubic cleavage face .	·00002014
2. At right angles to an artificial octohedral face . . .	·00002014
Iron pyrites (cubic):	
1. At right angles to a natural cubic face .	·00000907
2. At right angles to an artificial face upon a group of crystals without any common direction . .	·00000908
Ruby copper ore (cubic):	
1. At right angles to a face of the rhombic dodecahedron . .	·00000093
2. At right angles to a face perpendicular to the last . . .	·00000093
3. At right angles to an artificial face on a group of crystals without any common direction . .	·00000093

		α_{40}
Zirkon (Siberia: quadratic) . . .	A	·0000443
	B	·0000233
	M	·0000304
	M_1	·0000303
Arragonite (right rhombic prism) .	A	·00003460
	B	·00001719
	C	·00001016
	M	·00002031
	M_1	·00002065
Topas (right rhombic prism)	A	·00000592
	B	·00000484
	C	·00000414
	M	·00000497
	M_1	·00000497
Felspar (monoclinic)	A	− ·000002004 − ·00000203
	B	+ ·00001907 + ·00001905
	C	− ·00000148 − ·00000151
Epidote (monoclinic)	A	+ ·000009133
	B	·00000334
	C	·00001086
Augite (monoclinic)	A	·000018856
	B	·00000272
	C	·00000791
Azurite (monoclinic)	A	·00001259
	B	·00002081
	C	− ·00000098
Gypsum (monoclinic)	A	·00004163
	B	·00000157
	C	·00002933

		Linear		Cubical		Expansion of Unit length between 0° and 100° = 100 × $\left(\alpha_{40} + 10\frac{\Delta\alpha}{\Delta\theta}\right)$
		α_{40}	$\frac{\Delta\alpha}{\Delta\theta}$	α_{40}	$\frac{\Delta\alpha}{\Delta\theta}$	
Plate-glass, from St. Gobain		·00000777	1,58	·00002331	4,74	·0007928
Diamond (cubic)		·00000118	1,44	·00000354	4,32	·000132
Ruby copper ore .		—	—	·00000279	6,30	
Emerald (Siberian beryl: hexagonal)	A	− ·00000106	1,14	·00000168	3,80	
	B	+ ·00000137	1,33			
	M	·00000057	—	—	—	
	M_1	·00000056	—	—	—	
Quartz (hexagonal) .	A	·00000781	1,77	·00003619	6,53	·0007987
	B	·00001419	2,38			·0014428
	M	·00001206	—	—	—	
Rutile (quadratic) .	A	·00000919	2,25	·00002347	4,45	
	B	·00000714	1,10			
Cassiterite (Saxony: quadratic)	A	·00000392	1,19	·00001034	2·71	
	B	·00000321	0,76			

Table continued.

		Linear		Cubical		Expansion of Unit length between 0° and 100° = 100 × $\left(\alpha_{40} + 10\frac{\Delta\alpha}{\Delta\theta}\right)$
		α_{40}	$\frac{\Delta\alpha}{\Delta\theta}$	α_{40}	$\frac{\Delta\alpha}{\Delta\theta}$	
Periclase (artificial: cubic)	—	—	—	·00003129	8,01	
Spartalite (United States: hexagonal)	A	·00000316	1,86	·00001394	4,32	
	B	·00000539	1,23			
Corundum (India: rhombohedral)	A	·00000619	2,05	·00001705	6,55	
	B	·00000543	2,25			
Specular iron (Elba: rhombohedral)	A	·00000829	1,19	·00002501	6,43	
	B	·00000836	2,62			
Senarmontite (Constantine, Algeria: cubic)	—	—	—	·00005889	1,71	
Arsenious oxide (artificial: cubic)	—	—	—	·00012378	20·37	
Spinels (cubic):						
1. Spinelle (Ceylon) ruby	—	—	—	·00001787	7,29	
2. Pleonast(Warwick)	—	—	—	·00001805	5,34	
3. Gahnite (Fahlun)	—	—	—	·00001766	5,19	
4. Kreittonite (Silberberg)	—	—	—	·00001750	5,31	
Silver iodide (fused: crystalline)	—	—·00000139	— 1,4	—·00000417	— 4,2	
„ „ (hexagonal crystals)	A	—·000003966	— 4,27	—·000002772	— 1,51	
	B	+·000000647	+ 1,38			
	M_1	—·000000924	— 0,503			
	M	—·00000093				
„ „ (amorphous precipitate, pressed)	A	—·0000016625	— 2,01	—·0000041075	— 4,77	
	B	—·0000012225	— 1,38			
	M	—·00000137	— 1,6			
Potassium chloride (cubic)	—	+·000038026	+ 5,15	+·000114078	+ 15,45	
Rock salt (cubic) .	—	·000040390	4,49	·000121170	13,47	
Sal ammoniac (cubic)	—	·000062546	29,75	·000187638	89,25	
Silver chloride (cubic)	—	·000032938	12,23	·000098814	36,69	
Potassium bromide (cubic)	—	·000042007	9,78			
Silver bromide (cubic)	—	·000034687	3,83			
Potassium iodide (cubic)	—	·000042653	16,76			
Mercuric iodide (quadratic: fused, crystalline)	—	·000023877	19,96			
Lead iodide (hexagonal: fused, crystalline)	—	·000033598	5,84			
Cadmium iodide (hexagonal: fused, crystalline)	—	·000029161	17,47			
Gas carbon . .	—	·00000540	1,10	·0000162	3,30	·000551
Graphite (Batongol) .	—	·00000786	1,01	·00002358	3,03	·000796
Anthracite (Pennsylvania)	—	·00002078	— 8,15	·00006234	— 24,45	·001996
Bituminous coal (Charleroy)	—	·00002782	2,95	·00008346	8,85	·002811
Paraffin (Rangoon, melting point 56°)	—	·00027854	99,26	·00083562	297,8	

Table continued.

		Linear		Cubical		Expansion of Unit length between 0° and 100° = 100 × $\left(\alpha_{40} + 10\frac{\Delta\alpha}{\Delta\theta}\right)$
		α_{40}	$\frac{\Delta\alpha}{\Delta\theta}$	α_{40}	$\frac{\Delta\alpha}{\Delta\theta}$	
Silicon (fused) . .	—	·00000763	1,69	—	—	·000780
Sulphur (Sicily) . .	M	·00006413	33,48	—	—	·006748
Selenium (fused) .	—	·00003680	11,15	—	—	·003792
Tellurium (fused) .	—	·00001675	5,75	—	—	·001732
Arsenic (sublimed, in confused crystals)	—	·00000559	4,32	—	—	·000602
Osmium (semi-fused).	—	·00000657	2,18	—	—	·000679
Ruthenium (semi-fused, porous)	—	·00000963	2,81	—	—	·000991
Palladium (hammered, annealed)	—	·00001176	1,32	—	—	·001189
Rhodium (semi-fused.	—	·00000850	0,81	—	—	·000858
Iridium (fused) .	—	·00000700	0,79	—	—	·000708
Platinum (fused) .	—	·00000899	0,78	·00002697	2,34	·000907
Platinum-iridium alloy platin. 0·9, irid. 0·1	—	·00000884	0,76	·00002652	2,28	·000892
Gold (fused) . .	—	·00001443	0,83	·00004329	2,49	·001451
Silver (fused) . .	—	·00001921	1,47	·00005763	4,41	·001936
Copper, native from Lake Superior	—	·00001690	1,83	·00005070	5,49	·001708
,, artificial .	—	·00001678	2,05	·00005034	6,15	·001698
Brass (copper 0·715, zinc 0·277, tin 0·003, lead 0·005	—	·00001859	1,96	·00005577	5,88	·001879
Bronze (copper 0·863, tin 0·097, zinc 0·040	—	·00001782	2,04	·00005346	6,12	·001802
Nickel (reduced by hydrogen, compressed)	—	·00001279	0,71	·00003837	2,13	·001286
Cobalt, ditto .	—	·00001236	0,80	·00003708	2,40	·001244
Iron (soft, used for electromagnets)	—	·00001210	1,85	·00003630	5,55	·001228
,, (reduced by hydrogen, compressed)	—	·00001188	2,05	·00003564	6,15	·001208
Meteoric iron (Caille)	—	·00001095	1,75	·00003285	5,25	·001113
Cast steel (French): hard	—	·00001322	3,99	·00003966	11,97	·001362
,, ,, annealed	—	·00001101	1,24	·00003303	3,72	·001113
,, (English): annealed	—	·00001095	1,52	·00003285	4,56	·001110
,, (gray) .	—	·00001061	1,37	·00003183	4,11	·001075
Bismuth (rhombohedrons of 87° 40′)	A	·00001621	2,09	·00004037	8,31	·001642
	B	·00001208	3,11			·001239
	M_1	·00001346	2,77			·001374
Antimony (rhombohedrons of 117°18′)	A	·00001692	− 0,94	·00003456	1,74	·001683
	B	·00000882	1,34			·000895
	M_1	·00001152	0,58			·001158
Tin (Malacca; compressed powder)	—	·00002234	3,51	·00006702	10,58	·002269
Indium (fused) . .	—	·00004170	42,38	·00012510	127,1	·004595
Lead (fused) . .	—	·00002924	2,39	·00005772	7,17	·002948
Thallium (fused) .	—	·00003021	11,41	·00009063	34,23	·003135
Zinc (distilled, compressed powder)	—	·00002918	− 1,27	·00008754	− 3,81	·002905
Cadmium ,, ,,	—	·00003069	3,26	·00009207	9,78	·003102
Aluminium (fused) .	—	·00002313	2,29	·00006939	6,87	·002336
Magnesium (fused) .	—	·00002694	6,84	·00008082	20,52	·002762

In order to save room, and to make the table easier to read, six or seven ciphers are left out before each of the numbers giving the values of $\frac{\Delta\alpha}{\Delta\theta}$, and a comma is used to mark the *eighth* decimal place: thus the numbers for plate-glass, namely 1,58 and 4,74, are to be read 0·0000000158 and 0·0000000474 respectively.

The values given above for α_{40} and $\frac{\Delta\alpha}{\Delta\theta}$ in the case of *diamond* indicate that this substance has a minimum volume (or maximum density) at −42°·3, and that below this temperature it expands as the temperature falls. In like manner, a maximum density is indicated for *cuprous oxide* at −4°·3, and for *emerald* at −4°·2. On the other hand, a maximum volume, or minimum density, is indicated for fused *silver iodide* at about −60°.

Fusion and Solidification. The latent heat of fusion of *water* has been determined by Bunsen (*Pogg. Ann.* cxli. 30) by means of his ice-calorimeter. In two experiments he obtained the values 80·01 and 80·04: mean 80·025. He has also determined the *specific gravity of ice* at 0° by a new process, and obtained in three experiments the values

0·91682, 0·91673, 0·91667; mean 0·91674.

Solubility of Salts.—According to Nordenskiöld (*Pogg. Ann.* cxxxvi. 309), the effect of temperature in modifying the solubility of such salts as crystallise from aqueous solution without water, even at low temperatures, can be expressed by the following formula:

$$\log_{10} S = a + bt + ct^2,$$

or

$$S = 10^{(a + bt + ct^2)},$$

in which S is the quantity of a salt which can be dissolved by 1 part of water at the temperature t without forming a supersaturated solution, and a, b, and c are constants depending on the nature of the salt. The values of these constants have been calculated by Nordenskiöld for several substances, with the following results:

Sodium chloride . .	$\log S = -0{\cdot}4484 + 0{\cdot}0105\left(\frac{t}{100}\right) + 0{\cdot}0319\left(\frac{t}{100}\right)^2$
Potassium chloride . ,,	$= -0{\cdot}5345 + 0{\cdot}379\left(\frac{t}{100}\right) - 0{\cdot}09\left(\frac{t}{100}\right)^2$
Ammonium chloride . ,,	$= -0{\cdot}5272 + 0{\cdot}5483\left(\frac{t}{100}\right) - 0{\cdot}1732\left(\frac{t}{100}\right)^2$
Barium chloride . . ,,	$= -0{\cdot}5084 + 0{\cdot}3413\left(\frac{t}{100}\right) - 0{\cdot}658\left(\frac{t}{100}\right)^2$
Sodium nitrate . . ,,	$= -0{\cdot}1364 + 0{\cdot}3892\left(\frac{t}{100}\right) - 0{\cdot}003\left(\frac{t}{100}\right)^2$
Potassium nitrate . ,,	$= -0{\cdot}8755 + 0{\cdot}2003\left(\frac{t}{100}\right) - 0{\cdot}7717\left(\frac{t}{100}\right)^2$
Barium nitrate . . ,,	$= -1{\cdot}2793 + 1{\cdot}2495\left(\frac{t}{100}\right) - 0{\cdot}4307\left(\frac{t}{100}\right)^2$
Potassium chlorate . ,,	$= -1{\cdot}4776 + 1{\cdot}7834\left(\frac{t}{100}\right) - 0{\cdot}5555\left(\frac{t}{100}\right)^2$
Potassium sulphate . ,,	$= -1{\cdot}1061 + 0{\cdot}8117\left(\frac{t}{100}\right) - 0{\cdot}3245\left(\frac{t}{100}\right)^2$
Potassium chromate . ,,	$= -0{\cdot}2219 + 0{\cdot}1741\left(\frac{t}{100}\right) - 0{\cdot}0445\left(\frac{t}{100}\right)^2$

The general law expressed by these formulæ may be thus stated: the rate at which the power of water at any given temperature to dissolve a salt varies with variation of temperature is inversely proportional to its power of dissolving the salt at that given temperature.

Vaporisation and Condensation. *Tension of Vapours.*—The relation between pressure, volume, and temperature may be represented, in the case of perfect gases, by the equation (iii. 45)—

$$\frac{pv}{a+t} = \text{constant},$$

where $a + t$ denotes the temperature counted from the absolute zero. It is known, however, from Regnault's experiments (cf. iii. 48), that the law expressed by this equation does not apply with absolute strictness to any known gas; but the same experiments have also proved that it represents with a very close approach to accuracy the behaviour of the permanent gases at moderate pressures. In the case of vapours, on the other hand, the relation between pressure, volume, and temperature differs very considerably from this law, though the difference becomes smaller and smaller as the temperature is raised and the pressure is diminished—that is to say, as the vapour is farther removed from the state of saturation. In the case of several vapours, the passage from the state of complete saturation to that of an approximately perfect gas has been made the subject of a detailed investigation by Herwig (*Pogg. Ann.* cxxxvii. 19 and 592; also cxli. 84). The general result of his observations may be thus stated: at any given temperature t, the product of the pressure p into the volume v, which is just sufficient to allow a given mass of a substance to evaporate (so that the whole exists as saturated vapour), bears a constant ratio to the square-root of the absolute temperature at which the evaporation takes place: that is,

$$pv = \kappa\sqrt{a + t},$$

if a is the absolute temperature of melting ice and κ a constant coefficient. But since, as has just been said, the product of pressure into volume gets more and more nearly constant at a given temperature as the vapour is farther removed from the state of saturation, or as its volume becomes greater, if we represent by PV the sensibly constant value which this product assumes at the temperature t, when the vapour is sufficiently expanded, we get, by combining the last equation with the expression $\mathrm{PV} = k(a + t)$ representing the law of perfect gases,

$$\frac{\mathrm{PV}}{pv} = c\sqrt{a + t},$$

c again being a constant numerical coefficient. Herwig found that this coefficient has a constant value, not only in relation to a given vapour at various temperatures, but that it has the same value, namely 0·0595, for all the vapours examined by him, which were *alcohol*, *chloroform*, *sulphide of carbon*, *ether*, *water*, and *bromide of ethylene*.

This law being once established, the volume occupied by a unit mass of any substance in the state of saturated vapour at a given temperature may be deduced from observations of the volume and pressure exerted at the same temperature by a known mass of the vapour when expanded sufficiently to behave as a sensibly perfect gas. Thus if s be the mass of vapour which occupies the volume v under the conditions named, we have, for the volume of the unit mass under like conditions,

$$v_1 = \frac{v}{s} = \frac{\mathrm{PV}}{0{\cdot}0595\sqrt{a + t}\,.\,p\,s}.$$

The numbers in the following tables, calculated by this formula from Herwig's experiments, give the volumes occupied at various temperatures by 1 gramme of each of the substances mentioned, when in the form of saturated vapour, and therefore exerting the maximum pressure corresponding to each temperature:

Pressure, Volume, and Temperature of Saturated Vapours.

Sulphide of Carbon							
t	8°·5	14°·2	20°·1	32°·0	35°·9	40°·0	50°·0
p	183·09	234·45	294·12	461·54	531·59	614·45	856·5
v_1	1244·8	983·2	791·9	514·8	450·1	392·3	285·6

Alcohol (containing a trace of water)								
t	23°·0	30°·5	36°·4	41°·9	47°·8	57°·8	62°·9	69°·9
p	50·23	77·58	108·0	144·7	196·5	315·8	396·83	537·63
v_1	7977·9	5237·9	3798·39	2828·9	2125·0	1342·7	1076·6	802·4

Pressure, Volume, and Temperature of Saturated Vapours (continued).

	Water					Chloroform		
t	40°·0	55°·0	69°·8	85°·0	95°·0	30°·4	39°·8	49°·8
p	54·95	17·81	230·23	430·55	629·59	243·08	354·77	514·07
v_1	1872.3	8929·2	4700·0	2534·1	1772·2	619·5	431·0	301·6

	Ether			Bromide of Ethylene		
t	18°·2	25°·0	35°·0	25°·0	35°·0	43°·0
p	405·16	530·16	769·73	474·8	689·5	904·0
v_1	598·1	461·2	323·7	350·7	245·9	189·9

The numbers in the second line of each table represent the observed maximum pressures measured in millimetres of mercury, and those in the third line represent in cubic centimetres the corresponding volumes of 1 gramme of the several vapours.

TABLE I. (see next page).

1 *Molecule of Acid ; a molecules of Sodium hydrate.*

Name of Acid	*a*					
	½	1	2	3	4	6
1. *Monobasic acids*:						
Hydrochloric	68·5	137	137			
Hydrobromic	68·5	137	137			
Hydriodic	68	137	137			
Hydrosulphuric	39	77	78			
Hydrofluoric	80	163	163			
Hydrocyanic	14	28	27			
Nitric	68	137	137			
Hypophosphorous . . .	77	152	153			
Metaphosphoric	71	144	—			
Formic	—	132	—			
Acetic	66	132	132			
2. *Bibasic acids*:						
Hydrofluosilicic	—	133	266	—	—	
Sulphuric	71	146	310	—	310	
Selenic	—	148	304	—	304	
Sulphurous	—	159	290	—	293	
Selenious	—	148	270	—	275	
Hyposulphuric	—	—	271	—	—	
Chromic	—	131	247	—	252	
Phosphorous	74	148	284	289	—	
Carbonic (aqueous solution) .	—	110	202	—	206	—
Boric	64	111	200	205	—	206
Silicic	32	43	52	—	54	—
Stannic	—	—	—	—	96	—
Oxalic	69	138	283	—	285	—
Succinic	—	124	242	—	244	—
Tartaric	—	124	253	258	—	—
3. *Tribasic acids*:						
Citric	—	124	250	382	—	416
Orthophosphoric	73	148	271	340	—	353
Arsenic	74	150	276	359	—	374
4. *Tetrabasic acid*:						
Pyrophosphoric	—	144	286	—	527	545

potassium cyanide. It is a heavy liquid, boiling in contact with water at 55°–58°; its vapour irritates the eyes and has a pungent odour, like that of benzoyl chloride. It is converted partially on standing, completely by repeated distillation with water, into a solid modification (H. Müller, *Chem. Soc. J.* [2] ii. 420).

ETHYLENE IODIDE, $C^2H^4I^2$, is easily obtained in large quantity by saturating a pasty mixture of iodine and absolute alcohol with ethylene gas, agitating, and repeatedly adding fresh portions of iodine; the iodine-solution decanted from the crystals first formed is again mixed with iodine and treated with ethylene. The ethylene iodide, after washing with cold alcohol, is quite pure (Semenoff, *Zeitschr. Ch. Pharm.* 1864, p. 673).

Ethylene iodide heated with *water* in an exhausted tube to 275° for fifteen hours, is decomposed into ethane, carbon dioxide, and free iodine:

$$7C^2H^4I^2 + 4H^2O = 6C^2H^6 + 2CO^2 + 7I^2.$$

The hydrogen liberated from the water by the carbon of the ethylene iodide, ($C^2H^4I^2 + 4H^2O = 6H^2 + 2CO^2 + I^2$), decomposes the ethylene iodide, according to the equation $C^2H^4I^2 + H^2 = C^2H^6 + I^2$ (Berthelot, *Ann. Ch. Phys.* [4] iii. 211).

Ethylene iodide is decomposed by *mercuric chloride* according to the following equations:

$$\begin{aligned} 16HgCl^2 + 6C^2H^4I^2 &= 6C^2H^4ClI + 3(2HgCl^2.HgI^2) + 7HgCl^2. \\ &= 6C^2H^4Cl^2 + 5(2HgCl^2.HgI^2) + HgI^2. \\ &= 6C^2H^3Cl^3 + 4(Hg^2Cl^2.HgI^2) + 2Hg^2I^2 + 6HCl. \end{aligned}$$

Decomposition according to equation 1, takes place at ordinary temperatures, the equation then becoming

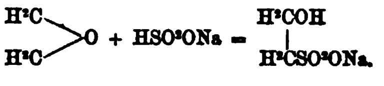
$$3HgCl^2 + 2C^2H^4I^2 = 2C^2H^4ClI + 2HgCl^2.HgI^2.$$

In fact, when an intimate mixture of 1 mol. $C^2H^4I^2$ and 3 mol. $HgCl^2$ is left to itself for some days, it becomes saturated with a red oil consisting of ethylene chloriodide, C^2H^4ClI (ii. 574). The decomposition represented by the second equation takes place when the mixture of $16HgCl^2$ and $6C^2H^4I^2$ is heated to 100°. Ethylene chloride is then obtained, mixed with a certain quantity of the chloriodide, the quantity of which may be diminished by rapid heating, but is always considerable (Maumené, *Compt. rend.* lxviii. 727; *Zeitschr. f. Chem.* [2] v. 366).

Iodethylene, C^2H^3I, heated in alcoholic solution to 100° with silver oxalate, yields silver iodide and a liquid decomposible by water, with formation of oxalic acid, probably an oxalic ether of vinyl alcohol, C^2H^3OH (Semenoff, *Zeitschr. Chem. Pharm.* 1864, p. 673).

ETHYLENE CHLORIODIDE, C^2H^4ClI, heated to 100°–200° in a sealed flask with 1 mol. moist silver oxide is converted in great part into ethylene alcohol, $C^2H^4(OH)^2$, both the chlorine and the iodine being replaced by hydroxyl. The same results are obtained with 2 mol. silver oxide. The chloriodide heated with water to 160°–220° is also converted into ethylene alcohol, hydrochloric acid, and hydriodic acid, which latter converts part of the ethylene alcohol into iodide. It appears from these results that the chlorine and iodine in the chloriodide are combined with the carbon in the same manner, and that it is not possible to replace one of them with hydroxyl without the other (Maxwell Simpson, *Phil. Mag.* [4] xxxv. 282).

ETHYLENE OXIDE, C^2H^4O, heated to 100° in a sealed tube with acid sodium sulphite is converted into the sodium salt of isethionic acid (Erlenmeyer, *Zeitschr. f. Chem.* [2] iv. 342):



ETHYLENE HYDROXYCHLORIDE, OR GLYCOLIC CHLORHYDRIN, $C^2H^4\left\{\begin{matrix}OH\\Cl\end{matrix}\right.$, is produced by direct combination of ethylene with hypochlorous acid, ClOH (Carius, *Ann. Ch. Pharm.* cxxvi. 195). The following mode of preparation is recommended by Butlerow (*ibid.* cxliv. 40). Glass flasks of the capacity of 30 litres or more are filled over water with ethylene gas. To prepare the hypochlorous acid, moist recently precipitated mercuric oxide (10 pts., containing about 4 pts. of the dry oxide, being taken for every litre of ethylene) is mixed with so much ice and water that the mixture shall contain 1 pt. oxide to 15 pts. water, and into this mixture, in a vessel standing in ice-water and in the dark, chlorine gas is slowly passed till the mercuric oxide has nearly disappeared. Half the original quantity of oxide is then added, and the whole is quickly poured into the flasks containing the ethylene, to 1, ½, ⅓, or ¼ molecule, according as the acid is monobasic, bibasic, tribasic, or tetrabasic respectively.

c. In the case of well-characterised acids, when the quantity of alkali or acid employed is more than is required to form the normal salt, the thermal effect of the excess is inconsiderable.

The only marked exceptions to these rules are presented by silicic acid (which gives no indication of possessing a definite basicity), boric acid, orthophosphoric acid, and arsenic acid.

The heat produced by the combination of several acids with potash, soda, and ammonia, in presence of excess of water, has been redetermined by Andrews (*Trans. Roy. Soc. Edinb.* xxvi. 85). His results are given in the following table, side by side with those which he obtained from similar measurements published in 1841, and are expressed in gramme-degrees of heat produced by the reaction of 1 molecular proportion of each alkali taken in grammes:

Heat produced by Acids and Alkalis (Andrews).

Acid	Potash		Soda		Ammonia	
	1870	1841	1870	1841	1870	1841
Sulphuric . .	16701	16330	16580	16483	14710	14135
Nitric . . .	14800	15076	14480	14288	12683	12440
Hydrochloric .	14940	14634	14744	14926	12964	12440
Oxalic . .	15124	14771	15032	14796	13088	12684
Acetic. . .	13805	14257	14000	14046	12316	12195
Tartaric . .	13508	13612	13400	13135	11744	11400

The quantity of heat generated by the combustion of *hydrogen*, or, more exactly, the quantity absorbed when 1 gramme of hydrogen at 0° and under 760 mm. pressure is produced by the decomposition of water at 0°, has been measured by Kiechl (*Jahresb.* 1869, p. 143), by comparing the heat evolved by an electric current in a voltameter during the decomposition of a known quantity of water, with that simultaneously evolved by the same current in a wire of resistance equal to that of the voltameter (comp. iii. 114). As the mean of nine determinations he obtained the number

33,591,

or, leaving out of account two results which differed considerably from the rest,

33,653.

From experiments on the direct combustion of hydrogen, Thomsen (*Zeitschr. f. Chem.* 1871, p. 181) finds 34,034 gramme-degrees to be the quantity of heat due to the formation of 18 grammes of water weighed *in vacuo*.

Determinations of the heat of combustion of various articles of food have been made by Frankland (*Phil. Mag.* [4] xxxii. 182; *Chem. Soc. J.* [2] vi. 33) by burning them under water with potassium chlorate, and deducting from the observed evolution of heat the amount corresponding to the decomposition of the chlorate. (See NUTRITION.)

Mechanical Equivalent of Heat. Several new determinations of the mechanical equivalent of heat have been made within the last eight or ten years. We give here a short statement of the physical principles involved in the various measurements, followed by a comparative table of the results.

Hirn's Determinations.—Four separate series of experiments for the determination of the mechanical equivalent of heat are described by G. A. Hirn (*Théorie mécanique de la Chaleur*, 1^{re} partie, pp. 55–75 : Paris, 1865).

1. The first series depended on the measurement of the quantity of heat produced by the expenditure of a known amount of work in overcoming the friction of liquids. The apparatus employed consisted of two concentric cylinders of brass, the inner one being 1 metre long and 0·3 metre in diameter, and the outer one large enough to leave everywhere between it and the smaller one a distance of 0·03 metre. The liquid to be experimented upon was caused to flow slowly through the cylindrical space thus formed, and the heat produced was estimated by measuring the change of temperature undergone by a known mass of the liquid during its passage through the

apparatus, proper allowance being of course made for the quantities of heat lost by radiation and conduction, or absorbed by the solid parts of the apparatus. The work expended was estimated by ascertaining the weight with which it was necessary to load friction-levers pressing against the ends of the outer cylinder in order to prevent it from being carried round by the force of friction acting between the liquid and the solid surfaces when the inner cylinder was made to turn at a known speed.

2. In the second series of experiments water was allowed to escape by a small opening from a cylinder where it was subject to a very high pressure, namely, 452,820 kilogrammes per square metre, and the elevation of temperature in the water was noted. In this experiment the actual energy with which the water escaped was very small, and was very quickly converted into heat in the receiving vessel, so that the work spent in heating each portion of the escaping water was that due to the fall of an equal mass through a height equal to that of the column of water required to produce the actual pressure employed.

3. In the third series the quantities measured were (*a*) the heat produced when a piece of lead was crushed by a blow, and (*b*) the mechanical energy spent in the blow.

4. The experiments of the fourth series consisted in observations of the change of pressure in a gas which was suddenly expanded without gaining or losing heat. Under these circumstances, the simultaneous changes of pressure and volume in a perfect gas are such as to fulfil the following equation:

$$\frac{p_1}{p_2} = \left(\frac{v_2}{v_1}\right)^k \quad . \quad . \quad . \quad . \quad . \quad (1),$$

where p_1 and v_1 represent the initial pressure and volume of the gas, p_2 and v_2 its final pressure and volume, and k the ratio of the specific heat under constant pressure to the specific heat under constant volume. During the change of volume, however, heat is either produced or absorbed; consequently the temperature of the gas changes, and the final pressure p_2 is different from what it would have been if the temperature had remained constant. Let p'_2 be the pressure corresponding to the final volume, supposing the temperature to have remained what it was at first: we then have, by Boyle's law—

$$\frac{v_2}{v_1} = \frac{p_1}{p'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

and, substituting this value in equation (1), we get $\frac{p_1}{p_2} = \left(\frac{p_1}{p'}\right)^k$, whence

$$k = \frac{\log p_1 - \log p_2}{\log p_1 - \log p'}.$$

The value of k obtained by Hirn, as the result of about forty experiments with air on this principle, has been already given (p. 669). This being known, the value of the mechanical equivalent is given by the formula

$$J = \frac{H\alpha}{Dc'(1 - \frac{1}{k})}$$

(comp. iii. 121), where α is the coefficient of expansion of air, c' the specific heat of unit mass of air, and D the mass of unit volume of air at 0° under the pressure H—quantities each of which is known from Regnault's experiments.

Joule's Determination (*Brit. Assoc. Rep.* 1867, pt. i. p. 512).—Joule has determined the value of the mechanical equivalent of heat by measuring the quantity of heat produced in a known time by an electric current of known strength traversing a metallic conductor of known resistance. The principle of the measurement is expressed by the formula

$$J = \frac{C^2Rt}{Q},$$

where Q is the quantity of heat produced in the time t by a current of the strength C in a conductor of resistance R, both C and R being expressed in absolute electro-magnetic measure. (See pp. 569–574.)

Violle's Determination (*Ann. Ch. Phys.* [4] xxi. 64).—When a conducting disc is made to revolve between the poles of a magnet, so that its plane of motion is perpendicular to the line joining the poles, electric currents are produced in the disc; and since these currents do not give rise to any external work, the energy represented by them is entirely converted into heat in the disc. At the same time, the induced currents and the magnet exert upon each other forces which oppose the motion of the disc, and consequently work must be continuously expended in order to keep up a constant speed of rotation. These phenomena have been made to serve as the basis of a determination of the mechanical equivalent of heat by Violle.

Regnault's Experiments (*Compt. rend.* lxvi. 209).—Besides the experiments above mentioned, which were undertaken for the special purpose of measuring the mechanical equivalent of heat, Regnault's recently published experiments on the velocity of sound in air may be mentioned here, since they give the data for fixing the ratio of the two specific heats of air, and hence the value of the mechanical equivalent. These experiments gave 330·3 metres per second as the velocity of sound in dry air at 0°, and consequently we have for the value of k (see iii. 41)—

$$k = v^2 \frac{s}{Hg\sigma} = 1{\cdot}393,$$

v being the velocity of sound in metres, g the acceleration due to gravity, σ the weight of unit-volume of mercury, and s the weight of unit-volume of air at 0° under a pressure equal to that of H metres of mercury.

The following table contains the results of the several investigations above mentioned:

Value of the Mechanical Equivalent of Heat.

Experimenter	Result	Method
Hirn . . .	432	Friction of water and brass.
„ . . .	433	Escape of water under pressure.
„ . . .	441·6	Specific heats of air.
„ . . .	425·2	Crushing of lead.
Joule . .	429·3	Heat produced by an electric current.
Violle . .	435·2 (copper) 434·9 (aluminium) 435·8 (tin) 437·4 (lead)	Heat produced by induced currents.
Regnault . .	437	Velocity of sound.

It will be remarked that, with one exception, all these values are perceptibly higher than that obtained by Joule from his experiments on the friction of water, and the single process which gave a result almost identical with the number commonly adopted on the strength of Joule's experiments is one which can hardly be made to give a very accurate value. As to the number deduced by Hirn from his experiments on the expansion of air (441·6), he points out that it is certainly too great, on account of the unavoidable errors of the method. Joule's new result is the lowest of three values obtained in distinct sets of observations, but it is adopted by him as the result of the investigation in consequence of more complete precautions to ensure accuracy having been taken in the set of experiments from which it was deduced than in the other two sets. These, however, were closely accordant with each other, and would lead to 431·5 as the value of the mechanical equivalent. Of the numbers obtained by Violle, the one in which he places the greatest confidence is that obtained by the experiments with a copper disc, and he places next the number obtained with a disc of aluminium.

Radiant Heat.

Emissive Power.—The following table gives the comparative emissive powers of the substances enumerated in it at 150°, according to Magnus's experiments (*Pogg. Ann.* cxxxix. 437).

Radiating Substance.		*Emissive power at* 150°.
Blackened silver	. . . .	100
Glass . .	2 mm. thick	64
Fluor-spar .	10 mm. „	45·5
Sylvin . .	3 mm. „	17
Rock-salt .	3 mm. „	13
Polished silver .	1 mm. „	9·7

When a plate of rock-salt was placed in front of a polished silver plate, either in contact or at a distance of 1 mm. from it, the radiation from both together was considerably more than the sum of their separate radiations (being as much as 41 per cent. of the radiation from the blackened silver plate when they were in contact). The cause of this effect was found to be the reflection by the silver plate of the heat radiated from the second surface of the rock-salt, for it was found to be greatly diminished when the silver plate was blackened and placed at the same distance from the rock-salt. Hence, as Magnus points out, the great importance, in all experiments upon the nature or amount of the radiation from diathermic substances like rock-salt, of avoiding as far as possible the presence of anything that can radiate or reflect heat through the substance under examination.

The difference between the radiating powers of the same substance, according as its surface is rough or polished, has been investigated by Magnus (*Pogg. Ann.* cxl. 337), whose experiments have proved that platinum which has been strongly hammered has the same emissive power as platinum which has been most carefully annealed, and also that when platinum-foil is passed, under great pressure, between a pair of rollers, one of which is smooth and the other covered with fine lines, the emissive power of the two surfaces of the foil is the same. Hence Magnus concludes that the power of emitting radiant heat has no direct connection with the greater or lesser *density* of the radiating surface (see v. 49). On the other hand, the radiating power of annealed platinum-foil may be doubled by scratching the surface with fine emery-paper; and by coating it with platinum-sponge, its radiating power may be increased sevenfold. In order to account for these results, Magnus supposes that, even in the case of metals, the origin of the heat radiated outwards is not only the geometrical surface, but also that the internal parts of the mass very near to the surface take part in the process; and that the greater radiating power of a rough surface, as compared with that of a smooth surface of the same material, is due to the fact that the irregularities of outline which constitute the roughening diminish in some manner the proportion of rays incident upon the outer surface from the interior which are there reflected back again into the mass.

Reflection.—The proportion in which the heat given out by various diathermic substances at 150° is reflected by surfaces of the same or of different kinds, and under various angles of incidence, has been investigated by Magnus (*Pogg. Ann.* cxxxix. 583). In these experiments, as well as in those to be mentioned presently, under the head *Transmission* (see p. 690), the substance which was employed as the source of the radiation was heated by being suspended by fine platinum wire in a current of heated air, so arranged with reference to a thermo-electric pile that not the smallest effect was produced upon the galvanometer except when a solid radiator was introduced into the current. The principal results of the investigation are given in the following table:

Reflection of Radiant Heat.

		RADIATING SUBSTANCES				
		Lamp-black * on silver	Glass	Rock-salt	Sylvin	Fluor-spar
Direct radiation, without reflection		124·5	119·8	21·5	35·5	63·0
Reflecting surface	Angle of Incidence	Percentage of total incident heat reflected				
Polished Silver . . .	33°	93·6	88·8	84·8	83·3	82·5
	45	94·4	89·4	89·4	92·6	86·0
	62	93·6	94·2	96·9	99·0	87·3
Glass	33	—	7·5	7·0	6·7	—
	45	8·4	8·6	9·3	9·2	11·0
	62	—	14·8	13·9	13·5	15·0
Rock-salt	33	—	7·6	6·0	6·5	4·9
	45	8·3	8·2	8·4	8·1	10·0
	62	—	12·9	12·8	10·8	11·7
Sylvin	33	—	2·6	4·6	2·7	2·7
	45	3·6	3·5	6·0	5·4	4·0
	62	—	8·5	10·7	8·9	10·8
Fluor-spar	33	—	7·2	23·0	15·4	6·5
	45	8·6	8·8	24·2	18·1	10·9
	62	—	14·3	33·5	24·3	12·4

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* The coating of lampblack was necessarily thin, as a thicker one did not adhere; it was probably not thick enough for the lampblack to produce its full effect.

It will be observed that, of the substances whose behaviour is given in this table, fluor-spar is the only one of which the reflecting power varies to any great extent with the nature of the source from which the heat comes. When the angle of incidence is 45°, the proportion of heat reflected varies—

With Silver, between 86 and 94·4 per cent.
„ Glass, „ 8·4 „ 11 „
„ Rock-salt, „ 8·2 „ 10 „
„ Sylvin, „ 3·5 „ 6 „

whereas fluor-spar reflects only 8·8 and 8·6 per cent. respectively of the heat radiated by lampblack and by glass, but as much as 24·2 per cent. of the heat from rock-salt, and 18·1 per cent. of that from sylvin.

Refraction.—The refraction of solar heat by sylvin (native potassium-chloride) has been compared by Knoblauch (*Pogg. Ann.* cxxxvi. 66) with its refraction by rock-salt. A beam of solar rays was allowed to pass through two slits, each 2 millim. wide, placed at a distance of 0·93 metre apart, and then through a prism, set at the angle of least deviation, 0·1 metre from the second slit, after which it fell upon a thermoelectric pile, with a linear opening 3 mm. wide. The following table gives the galvanometer-deflections produced by this arrangement of apparatus with a prism of sylvin of refracting angle = 50°, compared with the deflections obtained with a prism of rock-salt of refracting angle = 45°:

Refraction by Sylvin and Rock-salt.

	Sylvin prism of 50°	Rock-salt prism of 45°
In the first zone beyond the Violet (up to the limit)	0·00	0·00
„ Violet	0·50	0·30
„ Indigo	0·55	0·35
„ Blue	0·60	0·45
„ Green	0·65	0·50
„ Yellow and Orange	1·00	1·00
„ Red (as far as the limit) . . .	2·00	2·00
„ *first* zone beyond the Red . . .	2·83	2·50
„ *second* „ „	1·75	1·25
„ *third* „ „	0·50	0·25
„ *fourth* „ „	0·00	0·00

In both cases the greatest heating effect occurs in the part of the spectrum which is less refrangible than the visible red.

The distribution of heating power in a solar spectrum produced by using a silver heliostat mirror and lenses and prisms of rock-salt has also been studied by P. Desains (*Compt. rend.* lxx. 985). The apparatus used gave an angular separation of about 3° 48′ between the ends of the visible spectrum, and the greatest heating effect was found on an average at an angular distance of 51′ from the bright red: sometimes, at eight in the morning, the maximum of heat was at 46′ only from the red; in other cases, at noon, it was as much as 54′ from the red. Possibly this difference is owing to the absorption of a considerable part of the least refrangible heat by the water existing in the atmosphere in the liquid state, as mist, which is commonly more abundant in the morning than it is at noon. The first table on p. 690 gives an analysis of the heat-spectrum for about 11 o'clock in the forenoon of April 20, 1870.

If a curve were drawn with abscissæ proportional to the numbers in the first column of this table, and ordinates proportional to the corresponding numbers in the third column, the area enclosed by any part of the curve, the ordinates of its extremities, and the axis of abscissæ would express the total heating effect of the part of the spectrum represented by the corresponding part of the axis of abscissæ. Compared in this way, the total heating effect of the *visible* spectrum is found to be about ⅓ of the heating effect of the whole spectrum.

Distribution of Heat in the Solar Spectrum.

Angular Distance	Colour	Comparative Heating Power
0′	Extremity of the Violet . . .	0
30′	Violet	5
2° 18′	Blue	10
3° 0′	Greenish Yellow	23
3° 30′	Bright Carmine	39
3° 48′	Extreme Red	51
4° 0′	Beyond visible Red . .	81
4° 18′		100
4° 24′		94
5° 0′		20
5° 12′		8
6° 0′		0

Transmission.—The transmission of radiant heat from various sources through various media has been examined by Magnus with special reference to the properties of rock-salt (*Pogg. Ann.* cxxxix. 431). The mean results of his most important measurements are given in the following table:

Substances through which the Heat was transmitted	Thickness	Sources of Heat (temperature in all cases, 150°)						
		Rock-salt			*Sylvin* 3 to 4 mm. thick (clear)	*Fluor-spar* 8·8 mm. thick (clear, colourless)	*Silver Chloride* 2·5 mm. thick	*Silver Bromid* 1 mm. thick
		2·5 to 3 mm. thick	15 mm. thick (not quite clear throughout)	18 mm. thick (quite clear throughout)				
Air . .		100	100	100	100	100	100	100
	mm.							
Rock-salt .	1	58·2	68·1	54·4	—	—	—	—
" . .	2	41·6	60·3	52·8	61·4	80·5	71·6	70·6
" . .	5	30·5	50·6	43·3	—	—	—	—
" . .	20	20·0	40·2	24·7	59·2	70·8	72·1	73·3
" . .	80	20·9	39·4	16·6	—	—	—	—
Sylvin . .	3	55·16	70·7	64·8	49·6	88·9	73·7	66·2
" . .	10	44·0	—	—	—	—	—	—
" . .	20	36·5	56·4	47·8	28·4	85·1	65·2	60·9
" . .	29·5	—	48·4	39·8	—	—	—	—
Fluor-spar .	2·8	8·3	17·3	3·3	58·7	19·2	51·6	53·1
" .	10	8·3	15·6	2·8	54·5	9·1	43·6	48·3
Silver chloride	0·6	64·0	62·0	62·5	62·5	67·8	59·3	58·9
"	3	47·4	47·4	48·7	36·7	54·6	41·3	37·0
Silver bromide	0·3	68·8	68·0	68·0	70·5	72·2	69·4	65·3
"	2·75	45·3	44·4	44·1	43·7	45·1	41·8	37·5
Selenium .	2·5	13·3	15·0	16·9	9·53	21·3	13·7	10·9

These numbers afford a striking illustration of the previously known fact (see v. o0), that diathermic substances absorb most readily rays emitted by other portions of the same substances; but they also bring out in a very remarkable manner the thermochroic character of *rock-salt*. This is best seen by examining the results relating to the thickest piece (18 mm.) of that material, the thickness and perfect purity of which caused the heat given out by it to exhibit the special characters peculiar to the substance in the highest degree. Of this heat, little more than one-half was able to pass through a plate of rock-salt 2 millimetres thick, and only one-sixth could pass through 80 millimetres of rock-salt; while nearly the whole of it (96·7 per cent.) was stopped by a plate of fluor-spar 2·8 millimetres thick. Hence, as Magnus pointed out, the characteristic properties exhibited by rock-salt in connection with radiant heat (see v. 62, 63, 66, 67) are not the result of its being really *athermochroic*, as was thought by Melloni, but of its being *monothermochroic*, that is to say, of its having the power to emit and to absorb (at temperatures not above about 150°) rays solely or nearly of one kind, and of these rays having been present only in very small proportions in the heat from the sources employed by Melloni and most other experimenters who have studied its action. It has already been pointed out that the heat given out by rock-salt is reflected to an exceptionally great extent by fluor-spar; this property, together with the very small proportion in which it is transmitted by fluor-spar, forms a marked difference between the thermal characters of rock-salt and those of sylvin, which in many respects they so closely resemble.

Polarisation.—1. *By Emission.* It was shown in 1849 by De la Provostaye and Desains that not only luminous heat emitted obliquely is polarised at right angles to the plane of emission, but that this is the case also with heat emitted by platinum at temperatures as low as about 230° (*Jahresb.* 1849, p. 48). Magnus in 1866 (*Pogg. Ann.* cxxvii. 600; *Fortschr. d. Phys.* xxii. 328) confirmed this result, so far as regards polished platinum, but found that the heat emitted by platinised platinum is not polarised. More recently (1868) Magnus examined the heat emitted by various surfaces at 100° (*Pogg. Ann.* cxxxiv. 45; *Ann. Ch. Phys.* [4] xv. 467), and found that the proportion of heat polarised at right angles to the plane of emission, contained in the total radiation in a direction making an angle of 35° with the surface, could be represented by the numbers given in the following table:

Radiating surface	Percentage of polarised heat	Radiating surface	Percentage of polarised heat
Tin-plate	27·6	Colza oil	5·64
Copper	22·4	Melted rosin . . .	7·26
Aluminium . . .	28·5	White wax . . .	7·3
Mercury	32·0	Glycerin	5·61
Glass, transparent . .	10·4	Paraffin	5·0
Glass, black . . .	12·4		

The analyser employed in these experiments was a black glass reflector set at an angle of 35° to the axis of the incident beam.

2. *By Reflection.* By employing as polariser a pile of 4 plates of rock-salt, each from 3 to 4 mm. in thickness and having about 50 square centim. of superficial area, and a similar pile as analyser, Desains (*Compt. rend.* lxiv. 1246; *Pogg. Ann.* cxxxiv. 472) succeeded in polarising the heat radiated by copper at 160°. When the planes of incidence of analyser and polariser were parallel, the galvanometer connected with the thermoelectric pile which received the heat from the analyser showed a deflection of 12°; when the planes of incidence were at right angles to each other, the deflection was 7°.

Conduction of Heat. The laws of the conduction of heat by *liquids* have been investigated by Guthrie (*Phil. Trans.* 1869, p. 637) by a method in which one of the chief causes of uncertainty in previous experiments on the same subject is got rid of. His apparatus consisted essentially of an air-thermometer with a conical reservoir of sheet brass; the base of the cone, formed by a flat plate of platinum, was placed uppermost, and a calibrated and graduated glass tube, open at both ends, was fitted into the apex of the cone by means of a cork. The lower end of this tube dipped into coloured water contained in a wide open vessel, and the motion of the water in the tube indicated the changes of temperature in the air in the conical reservoir. A similar brass cone with a flat platinum base was placed, base downwards, with its axis in the same vertical line as that of the thermometer-cone, with its base facing the base of the latter at a distance which could be accurately adjusted and measured by means of a micrometer screw. The apparatus being set so that the bases of the two cones were exactly horizontal, the upper one was brought down to within the required distance (usually 1 or 2 millimetres) of the lower one, and the flat cylindrical space between the two platinum faces was filled by means of a pipette with the liquid to be examined. By this arrangement a uniform layer of liquid was obtained, the vertical sides of which were not in contact with any solid material which could either help or hinder the passage of heat from one surface to the other. Heat was applied to the upper surface of this layer of liquid, by causing a stream of warm water of known temperature to flow through the upper cone; and the passage of heat through it was judged of by comparing the resulting depression of the coloured water in the thermometer-tube with the depression which occurred, under otherwise like conditions, when the faces of the two cones were close together, contact between them being made more perfect by wetting them with mercury. The numbers in the following table express the relative *resistances* to the passage of heat through the various liquids examined by him, which Guthrie deduced from the results of his experiments made under the following conditions: namely, temperature of the air 20·17°, temperature of water in the upper cone 30·17°, thickness of layer of liquid 1 millim., duration of each experiment 1 minute:

Liquid	Thermal resistance	Liquid	Thermal resistance
Water	1·0	Amylic acetate . . .	10·00
Glycerin	3·84	Amylamine . . .	10·14
Acetic acid (glacial) . .	8·38	Amylic alcohol . . .	10·23
Acetone	8·51	Oil of turpentine . .	11·75
Ethylic oxalate . . .	8·85	Butylic nitrate . . .	11·87
Sperm oil	8·85	Chloroform	12·10
Alcohol	9·09	Bichloride of carbon . .	12·92
Ethylic acetate . . .	9·09	Mercury-amyl . . .	12·92
Nitrobenzene . . .	9·86	Bromide of ethylene . .	13·16
Amylic oxalate . . .	10·00	Amylic iodide . . .	13·27
Butylic alcohol . . .	10·00	Ethylic iodide . . .	14·20 (?)

It can hardly be supposed that the method employed in these experiments could give strictly accurate numerical results, though the sources of error cannot have been such as to cause any great error in simply comparative measurements. Hence we do not reproduce here the numbers calculated by Professor Guthrie to express the 'number of heat-units arrested in 1 minute by 1 square decimetre 1 millim. in thickness' when the temperature of the lower surface of the layer of liquid is 20·17, and that of the upper surface 10° higher. One of the most important results of this investigation is that the conducting power of liquids for heat is greater at high temperatures than at low ones.

Conducting Power of Metals.—Some confusion exists in the statements in vol. v. (pp. 69–72) with regard to the conducting power of metals, caused partly by the variety of units adopted by different experimenters for the purpose of expressing their results. It will therefore be useful to repeat the statement of some of the numerical values in such a way as to prevent the possibility of further error. In the first place, however, it is needful to correct a statement made in p. 69 (vol. v.) to the effect that coefficients of conducting power are expressed by the same number, whether they are referred to the *kilogram*, *millimetre*, and *square metre*, or to the *gram*, *centimetre*, and *square centimetre*, as units of mass, thickness, and area respectively. If we denote by Q the quantity of heat which would pass per second through a plate 1 mm. thick and 1 square metre in area, with a given difference of temperature between the surfaces, the quantity which would pass under like conditions through each square centimetre of a plate 1 centim. thick would be $\frac{Q}{10 \times 10{,}000}$, since the thickness, in the second case, would be ten times as great, and the area 10,000 times as small, as in the first case; but if this smaller quantity of heat is expressed in gram-degrees instead of in kilogram-degrees, the number representing it will be 1,000 times as great: hence it appears that, in order to convert coefficients of conductivity expressed in *kilogram-degrees*, per *square metre*, per *millimetre*, per *second*, into *gram-degrees*, per *square centimetre*, per *centimetre*, per *second*, we must multiply by $\frac{1{,}000}{10 \times 10{,}000} = 0{\cdot}01$. Further, if the *minute* be taken as the unit of time, instead of the second, we must multiply again by 60, so that to pass from kilogram-degrees, per square metre, per millim., per second to *gram-degrees*, per *centimetre*, per *minute*, we must *multiply by* 0·6. We pass now to the statements of experimental results.

Péclet (*Traité de la Chaleur*, 3rd edit. vol. i. pp. 390, 391) gives the following as the result of a determination of the absolute conducting power of lead: the quantity of heat which would pass in 1 hour through a plate of lead 1 sq. metre in area and 1 metre thick, with a difference of 1° between the temperature of its surfaces, is 13·83 kilogram-degrees. This result, reduced to what it would be for a plate 1 millim. thick and for 1 second of time, would become (compare v. 69)

$$13·83 + \frac{1,000}{3,600} = 3·84.$$

Ångström (*Pogg. Ann.* cxiv. 527) gives, as the results of his experiments on copper and iron, the numbers 54·62 and 9·77 respectively as the numbers of gram-degrees which would pass per *second* through each square centim., of plates 1 centim. thick, and at a mean temperature of from 51° to 52°, if the temperature of the surfaces differed by 1 degree. From the context, however, it appears that 1 *second* here is a mistake for 1 *minute*. In a subsequent paper (*Pogg. Ann.* cxviii. 429) Ångström gives the following values for the conductivities of copper and iron at the temperature $t°$:

$61·63\,(1-0·00214t)$.	copper (first specimen).
$58·94\,(1-0·001519t)$.	„ (second specimen).
$11·927\,(1-0·002874t)$.	iron.

Neumann (*Ann. Ch. Phys.* [3] lxvi. 185) takes as his units of time and length 1 minute and 1 Paris line, and, as unit of heat, the quantity required to raise the temperature of 1 cubic line of water 1 degree, and adds that to reduce his values to the units employed by Péclet or to those employed by Ångström, they must be multiplied by 0·0848 or by 0·0509 respectively. The following are the results which he gives:

Copper . . .	1306
Brass . . .	356
Zinc . . .	362
German silver . .	129
Iron	193

These various results, expressed according to the same units, are collected in the following table, where the numbers in the columns headed A are referred to 1 gram-degree as the unit of heat, 1 centimetre as the unit of length, and 1 minute as the unit of time, whereas for the columns headed B the units are 1 kilogram-degree, 1 millimetre, 1 square metre, 1 second:

	Ångström		Neumann	
	A	B	A	B
Copper . .	$61·63\,(1-0·00214t)$ $58·94\,(1-0·001519t)$	$102·7\,(1-0·003567t)$ $98·23\,(1-0·002532t)$	66·48	110·75
Zinc . .	. . . . .	. . . . .	18·43	30·70
Brass . .	. . . . .	. . . . .	18·12	30·19
Iron . .	$11·927\,(1-0·002874t)$	$19·88\,(1-0·00479t)$	9·82	16·37
German silver	. . . . .	. . . . .	6·57	10·94
Lead . .	(A) 2·30 ; (B) 3·84 . . .	Péclet.		

The numbers given at p. 72, vol. v., as the result of Neumann's experiments on several non-metallic substances refer to the units employed in the columns B of the above table. G. C. F.

HELENIN. According to Hoyer (*Vierteljahrs. pr. Pharm.* xiii. 544), the formula of this substance is $C^{16}H^{14}O^{5}$, which, however, requires 12·8 p. c. carbon and 0·8 p. c. hydrogen more than the formula $C^{21}H^{28}O^{3}$, deduced by Gerhardt (iii. 188) from several closely agreeing analyses. According to Hoyer, helenin melts at 75°; according to Gerhardt, at 72°.

HELIANTHUS. The seeds of the sunflower (*H. annuus*) yield 21·8 p. c. of fixed oil (Cloez, *Bull. Soc. Chim.* [2] iii. 41).

The tubers of Jerusalem artichoke (*H. tuberosus*) gathered in September yield a juice which is strongly lævogyrate, is only partially thrown into alcoholic fermentation by beer-yeast, and when left to itself solidifies to a curdy mass, with separation of inulin. The juice expressed therefrom deposits a further quantity of inulin on addition of alcohol; after the separation of the inulin it is optically inactive, and ferments with yeast without becoming optically active. The tubers taken up in March or April yield a dextrogyrate juice, which is free from inulin, and yields by fermentation a considerable quantity of alcohol. After evaporation it yields, on addition of alcohol, a gummy precipitate, the aqueous solution of which is optically inactive, and ferments without alteration of this property (*vid. inf.*). The alcoholic solution separated from this gummy substance is dextrogyrate, and undergoes, under the influence of acids or of yeast, the same transformation as cane-sugar, yielding inverted sugar, with a rotatory power varying according to temperature. The alcoholic solution when evaporated leaves a syrup, from which, by treatment with baryta and decomposition of the resulting precipitate with carbonic acid, crystallisable cane-sugar is obtained. The tubers gathered in September yield neither sugar nor a saccharate when thus treated. Hence it appears that the inulin formed in the early stage of growth is afterwards converted into crystallisable cane-sugar and an uncrystallisable optically inactive sugar (Dubrunfaut, *Compt. rend.* lxiv. 764).

Ville a. Joulie (*Bull. Soc. Chim.* [3] vii. 262), by repeatedly treating the juice of Jerusalem artichoke tubers with alcohol, obtained a substance which they designate as levulin; it resembles dextrin, has a sweetish taste, is soluble in water, reduces alkaline cupric solutions only after boiling with acids, is optically inactive, but becomes strongly lævogyrate by treatment with hydrochloric acid.

HELICIN. $C^{13}H^{16}O^7$.—This compound, the glucoside of salicylol, is converted by digestion in aqueous solution with excess of sodium-amalgam into salicin, $C^{13}H^{18}O^7$ (Lesenko, *Zeitschr. Chem. Pharm.* 1864, p. 577). According to Swarts (*Institut.* 1865, p. 325), helicin thus treated yields helicoïdin, $C^{26}H^{34}O^{14} = 2C^{13}H^{16}O^7 + H^2$.

Helicin treated with chlorides of acid radicles yields substitution-products (Schiff, *Zeitschr. f. Chem.* [2] v. 1). Acetyl chloride decomposes it even at ordinary temperatures; and if the action be allowed to go on for 24 hours, the mixture then heated to 60° and mixed with ether, *tetracetyl-helicin*, $C^{13}H^{12}(C^2H^3O)^4O^7$, is dissolved, and may be obtained by crystallisation from alcohol in shining prisms. Boiled with absolute alcohol, it yields ethyl acetate. By boiling it with water and magnesia, the whole of the acetyl is removed as magnesium acetate.

Helicin heated to 60° with benzoyl chloride, is converted into *benzoyl-helicin*, $C^{13}H^{15}(C^7H^5O)O^7$, which separates as a white crystalline powder, insoluble in ether, slightly soluble in water and in alcohol, and converted by treatment with water and sodium-amalgam containing a small proportion of sodium, into populin (benzoyl-salicin). Helicin heated with benzoyl chloride to 150°–170° yields *tetrabenzoyl-helicin*, $C^{13}H^{12}(C^7H^5O)^4O^7$, coloured brown by secondary products, and difficult to purify. It is soluble in alcohol and ether, nearly insoluble in water, and when heated in a sealed tube with hydrochloric acid, gives up the whole of its benzoyl as benzoic acid.

Helicin reacts with organic bases like an aldehyde, exchanging an atom of its oxygen for an imidogen group in which the hydrogen is replaced by an alcohol-radicle, *e.g.* $(NC^5H^{11})''$, $(NC^6H^5)''$, &c. Amylamine and aniline act upon it at ordinary temperatures, toluidine only at the boiling heat. The *phenyl-derivative* $C^{19}H^{21}NO^6 = C^{13}H^{16}O^6(NC^6H^5)''$ is prepared by gently heating helicin with aniline, treating the product several times with acetic acid to remove the excess of aniline, dissolving the yellow residue in alcohol, adding an equal volume of ether, filtering, evaporating, dissolving in absolute alcohol, and pouring the filtered solution into excess of cold water. The aniline derivative of helicin, $C^{19}H^{21}NO^6$, then separates as a yellow powder, which turns green on exposure to the air, is insoluble in water, very soluble in alcohol, and forms with concentrated acids, scarlet solutions which are decomposed by water. The hydrochloric solution does not yield a platinochloride. By boiling with acids or alkalis it is resolved into glucose and salhydranilide, $C^7H^6O(NC^6H^5)$, which latter is then further resolved into its constituents. The *toluidine-derivative* of helicin is similar in every respect to the aniline derivative (Schiff, *Zeitschr. f. Chem.* [2] iv. 638).

The acetyl and benzoyl derivatives of helicin gently heated with aniline and toluidine yield similar derivatives. *Tetracetohelicinanilide*, $C^{13}H^{12}(C^2H^3O)^4O^6(NC^6H^5)$, separates from solution in hot alcohol as a white crystalline powder. A similar compound is formed with toluidine. The anilide heated to about 160° with toluidine yields *tetracetohelicinanilotoluide*, $C^{13}H^{12}(C^2H^3O^4)O^5(NC^6H^5)(NC^7H^7)$, and with aniline a similar compound containing 2 at. NC^6H^5. Both these compounds are amorphous, and when boiled with water and magnesia give up 2 at. acetyl in the form of magnesium acetate, while the other two are separated as acetanilide and acetotoluide. Benzoyl-helicin and tetrabenzoyl-helicin yield analogous compounds with aniline and toluidine (Schiff, *ibid.* [2] v. 51).

HELLEBORIN, $C^{36}H^{42}O^{6}$, and **HELLEBOREÏN**, $C^{26}H^{44}O^{15}$ (Husemann a. Marmé, *Ann. Ch. Pharm.* cxxxv. 55).—Two glucosides existing in the roots of *Helleborus niger* and *H. viridis* and determining their physiological action. Helleborin, which occurs but very sparingly in black, more abundantly in green hellebore, is identical with the supposed azotised body *helleborine*, obtained in an impure state from black hellebore by Bastick (iii. 140). Helleboreïn is much more abundant in black than in green hellebore, but occurs in considerably larger quantity than helleborin, even in the latter.

To prepare helleboreïn, the aqueous decoction of the root is precipitated with basic lead acetate; the concentrated filtrate is freed from excess of lead by sodium sulphate and phosphate; the precipitate, after being repeatedly pressed, is stirred up with alcohol and levigated litharge, dried therewith, and exhausted with boiling alcohol; and the helleboreïn is precipitated from the strongly concentrated extract by ether. After repeated solution in alcohol and precipitation with ether, it crystallises gradually from the former in transparent nodular groups of microscopic needles, which on exposure to the air crumble to a yellowish-white hygroscopic powder. It has a sweetish taste, is very soluble in water, somewhat less soluble in alcohol, and quite insoluble in ether. The aqueous solution, which scarcely reddens litmus, dries up to an amorphous yellowish mass, which loses its water at 110°–120°, and then exhibits the composition above given, becomes straw-yellow above 160°, brown at 220°–230°, viscid at 280°, and then carbonises. Strong sulphuric acid dissolves it, with brown-red colour, gradually changing to violet. Alkalis and alkaline earths have no action upon it. By boiling with dilute acids, it is resolved into helleboretin, $C^{14}H^{20}O^{3}$, which separates as a dark violet-blue precipitate, and glucose, which remains dissolved:

$$C^{26}H^{44}O^{15} = C^{14}H^{20}O^{3} + 2C^{6}H^{12}O^{6}.$$

Helleboretin when dried forms a grey-green, amorphous, inodorous, and tasteless powder melting above 200°, insoluble in water and ether, but easily soluble, with violet colour, in alcohol. From the brown-red solution in strong sulphuric acid it is precipitated by water in its original state.

Helleborin, $C^{36}H^{42}O^{6}$, is best prepared from old roots of green hellebore. The hot-prepared and strongly concentrated alcoholic extract is repeatedly agitated with boiling water; the liquid freed from supernatant fatty oil is evaporated; and the helleborin which separates on cooling is washed with water and purified by recrystallisation from alcohol. It forms shining, white, concentrically grouped needles, insoluble in cold water, slightly soluble in ether and in fixed oils, easily soluble in boiling alcohol and chloroform; decomposes when heated above 250°. The smallest trace of it may be detected by its reaction with strong sulphuric acid, which first colours it deep red, and then dissolves it with the same colour. It is a stronger narcotic than helleboreïn, and its alcoholic solution has a very acrid burning taste. It is resolved by boiling with dilute acids, or more completely with a concentrated solution of zinc chloride, into glucose and helleboresin, $C^{30}H^{38}O^{4}$:

$$C^{36}H^{42}O^{6} + 4H^{2}O = C^{30}H^{38}O^{4} + C^{6}H^{12}O^{6}.$$

The helleboresin separates as a resinous body which is insoluble in water, slightly soluble in ether, easily soluble in boiling alcohol, and is separated therefrom by water as a white flocculent precipitate.

HEMIPINIC ACID. $C^{10}H^{10}O^{6}$.—This acid is produced by oxidising opianic acid ($C^{10}H^{10}O^{5}$) with chromic acid mixture (Matthiessen, *Proc. Roy. Soc.* xvii. 341). It crystallises in different forms with ½, 1, or 2½ mol. water; the first and second of these hydrates crystallise in the monoclinic system (Matthiessen a. Foster, *ibid.* xvi. 40). Respecting its reactions with hydriodic and hydrochloric acids, see iii. 142. It is not reduced to opianic acid or meconin by any reducing agents; neither have experiments to form opianic acid by the union of hemipinic acid and meconin been successful; nor has hemipinic acid been oxidised to any other compound. Heated to 170° it gives off water and leaves an anhydride, $C^{10}H^{8}O^{5}$, which may be crystallised unaltered from absolute alcohol, but when treated with ordinary spirit of 90 p. c. it forms ethylhemipinic acid, $C^{10}H^{9}(C^{2}H^{5})O^{6}$ (Matthiessen a. Wright, *ibid.* xvii. 341).

HEMP. See CANNABIS.

HEPTANE. *Septane. Heptyl Hydride.* $C^{7}H^{16}$.—The properties of this hydrocarbon, obtained from various sources, and of its derivatives $C^{7}H^{14}$, $C^{7}H^{15}Cl$, &c., have been examined by Schorlemmer (*Proc. Roy. Soc.* xiv. 164, 464). The specific gravities and boiling points are given in the following table:

Formula		Heptyl-compounds from :			
		Petroleum	Azelaic acid	Ethyl-amyl	Methyl-hexyl
C^7H^{16}	Boiling point Sp. gr.	98° (91°) 0·7149 at 15·5°	100·5° 0·6840 at 20·5°	90·5° 0·6819 at 18·5°	90° 0·6789 at 19°
C^7H^{14}	Boiling point Sp. gr.	96° 0·7383 at 17·5°	96° 0·7026 at 19°	94° 0·7060 at 12·5°	
$C^7H^{15}Cl$	Boiling point Sp. gr.	149° 0·8965 at 19°	152° 0·8737 at 18·5°	147° 0·8780 at 18·5°	
$C^7H^{16}O$	Boiling point Sp. gr.	164·5° 0·8749 at 16°	165·5°? 0·8286 at 19·5°	164° 0·8291 at 13·5°	
$\left.\begin{matrix}C^7H^{15}\\C^2H^3O\end{matrix}\right\}O$	Boiling point Sp. gr.	180° 0·8868 at 19°	181° 0·8605 at 16°	179° 0·8707 at 16·5°	

The ethyl-amyl $C^2H^5.C^5H^{11}$ was prepared by decomposing a mixture of ethyl and amyl iodides with sodium, treating the product with a mixture of nitric and sulphuric acids, and rectifying over sodium. The *heptyl chloride*, $C^7H^{15}Cl$, prepared from it, was resolved (like that obtained from petroleum heptane, iii. 146), by heating to 160°–180° with potassium acetate and acetic acid, into heptylene and heptyl acetate. The *heptyl alcohol*, $C^7H^{16}O$, prepared from this acetate, dissolves in strong sulphuric acid, with slight browning, and formation of a sulpho-acid whose barium and calcium salts are not crystallisable. By oxidation with chromic acid mixture, it yields œnanthylic acid, together with a little œnanthol: hence it is a primary alcohol. Heptane prepared by heating azelaic acid with baryta, $C^9H^{16}O^4 = C^7H^{16} + 2CO^2$ (Dale, *Chem. Soc. J.* [2] ii. 258), yields by a similar series of reactions, a primary alcohol boiling at 94°. The portion of American petroleum boiling below 100° yields, together with the heptane boiling at 98°, another isomeric hydrocarbon boiling at 90°–92° (see also Warren, *Jahresb.* 1865, p. 516). The heptanes from azelaic acid and ethyl-amyl are regarded by Schorlemmer as distinctly isomeric. The former is probably the normal compound $CH^3—(CH^2)^5—CH^3$; the latter, if prepared from ordinary amyl-iodide (p. 111), must be supposed to contain the group $CH(CH^3)^2$: hence its constitutional formula is probably $CH^3—(CH^2)^3—CH(CH^3)^2$.

Phthalic and terephthalic acids heated with 80 pts. of saturated hydriodic acid yield heptane boiling at 91°–93°:

$$C^8H^6O^4 + 14HI = C^7H^{16} + CO^2 + 2H^2O + 7I^2.$$

Toluene, C^7H^8, similarly treated, is completely converted into heptane; benzoic acid also yields the same hydrocarbon as normal product, together with hexane, C^6H^{14}, in consequence of the previous splitting up of part of the benzoic acid into benzene and carbon dioxide (Berthelot, *Jahresb.* 1867, pp. 346, 350). Toluidine and paratoluidine heated with 60 pts. hydriodic acid are almost wholly resolved into ammonia and heptane (Berthelot, *Compt. rend.* lxviii. 606): $C^7H^9N + 10HI = NH^3 + C^7H^{16} + 5I^2$.

Heptane boiling at 97·8° is found, together with heptylene, C^7H^{14}, amongst the hydrocarbons produced by the dry distillation of the lime-soap of Menhaden oil (Warren a. Storer, *Zeitschr. f. Chem.* [2] iv. 231).

HEPTINE or *Septine*, C^7H^{12}, also, but inappropriately, called *Œnanthylidene*. —A hydrocarbon homologous with ethine or acetylene, first obtained by Limpricht (*Jahresb.* 1857, p. 465); more completely examined by Rubien (*Ann. Ch. Pharm.* cxlii. 224). It is obtained by boiling heptylene chloride, $C^7H^{14}Cl^2$ (iii. 148), with 2 vol. concentrated alcoholic potash for twelve hours in a retort with upright condenser, treating the product with water, rectifying, collecting the chloroheptylene, $C^7H^{13}Cl$, which distils above 120°, and repeatedly heating it to 150° in sealed tubes, with alcoholic potash. On subjecting the portion of the oily product which boils below 120° to repeated fractional distillation, heptine is ultimately obtained as a transparent, colourless, mobile liquid, boiling at 106°–108°. It has an intensely alliaceous odour, is lighter than water, burns with a smoky flame, and dissolves easily in alcohol, ether, and benzol. Bromine acts violently on it in diffused daylight, forming the dibromide $C^7H^{12}Br^2$; with excess of bromine in sunshine the tetrabromide $C^7H^{12}Br^4$ is produced, which, when purified, is a yellowish oil, smelling like fennel, not volatile without decomposition, easily soluble in ether and benzol, sparingly in alcohol. Heated with sodium it decomposes and takes fire. On boiling it with alcoholic potash, potassium bromide is slowly deposited, and an oil is formed having a faint alliaceous odour.

HEPTYLIDENE. C^7H^{14}.—A diatomic radicle related to heptylene in the same manner as ethylidene to ethylene. Several diamines containing it have been obtained by Schiff (*Ann. Ch. Pharm. Suppl.* iii. 343). *Triheptylidene-diamine*, $C^{21}H^{42}N^2 = (C^7H^{14})^3N^2$, is formed, with separation of water, &c., on passing dry ammonia gas into anhydrous œnanthol: $3C^7H^{14}O + 2NH^3 = 3H^2O + (C^7H^{14})^3N^2$. It is a yellow aromatic oil, which distils undecomposed above 400°, and does not unite either with acids or with chlorides. It is also formed on agitating œnanthol with aqueous ammonia, or heating it with ammonium carbonate and acetate. *Diœnanthylidene-diamyl-diamine*, $C^{24}H^{50}N^2 = (C^7H^{14})^2(C^5H^{11})^2N^2$, produced by mixing œnanthol with amylamine, is an oily liquid which distils with partial decomposition. Several phenyl-diamines containing heptylidene are described under PHENYLAMINES (iv. 458).

HERACLEUM. The volatile oil obtained from the fruits of the cow-parsnep (*Heracleum sphondylium*, L.) by distillation with water (80 lb. of the fresh ripe fruits yielding about 120 grms. of the oil) is light green, mobile, has a sp. gr. of 0·864 at 20°, a faint, not unpleasant odour, and a sharp burning taste. It consists mainly of octyl acetate, $C^2H^3O^2.C^8H^{17}$, which may be obtained pure by continued fractionation of the portion of the oil passing over between 200° and 212°. This ether yields by saponification a primary octyl alcohol, $C^8H^{18}O$, boiling at 190°–192°, and yielding, by oxidation with chromic acid, an acid, $C^8H^{16}O^2$, identical or isomeric with the capric acid of natural fats. (See OCTYL ALCOHOLS.)

The portion of the crude oil distilling between 190° and 195° consists mainly of the same octyl alcohol. The higher fractions yield by continued fractional distillation an ethereal liquid boiling between 268° and 271°, and consisting mainly of octyl caproate, $C^6H^{11}O^2.C^8H^{17}$. The acid $C^6H^{12}O^2$ obtained from this ether by saponification is identical with the caproic acid obtained from natural fats. The acid water obtained in the distillation of the fruits contains acetic and caproic acids (Zincke, *Ann. Ch. Pharm.* clii. 1).

HERSCHELITE. According to V. von Lang (*Phil. Mag.* [4] xxviii. 506), the crystals of this mineral, hitherto regarded as hexagonal (iii. 150), are polysynthetic, being composed of six individuals belonging to the rhombic system and united by the faces ∞P.

HESSENBERGITE. A silicate of unknown composition, occurring in very small tabular crystals on the so-called 'Eisenrosen' from the Fibia on the St. Gothard. According to Kenngott (*Jahresb.* 1863, p. 802), they belong to the rhombic system; according to Hessenberg (*ibid.* 1866, p. 924), they are monoclinic.

HEXADECYL. $C^{16}H^{33}$.—Syn. with CETYL.

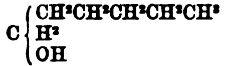
HEXAHENE. C^6H^4.—A hydrocarbon obtained, together with others, by heating naphthalene with excess of silver oxide (Maumené, *Bull. Soc. Chim.* [2] vii. 72).

HEXAMETHYLENAMINE. See METHYLENE-COMPOUNDS.

HEXANE, SEXTANE, or **HEXYL HYDRIDE,** C^6H^{14}, is produced by the action of hydriodic acid at 280° on benzene: $C^6H^6 + 8HI = C^6H^{14} + 4I^2$ (Berthelot, *Jahresb.* 1867, p. 345); also by heating suberic acid with lime or baryta: $C^8H^{14}O^4 = C^6H^{14} + 2CO^2$. The latter product has the same specific gravity as the β hexyl hydride of Wanklyn a. Erlenmeyer (Dale, *Chem. Soc. J.* [2] ii. 258). Hexane is also found among the hydrocarbons of Menhaden oil (p. 696). Hexane, like all the paraffins, is but slowly attacked by potassium permanganate, yielding a mixture of fatty acids apparently containing caproic acid (Berthelot).

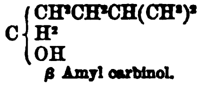
HEXINE. C^6H^{10}. *Sextine. Hexoylene.*—A hydrocarbon, homologous with acetylene, and isomeric with diallyl (p. 92), produced by heating bromhexylene, $C^6H^{11}Br$, to 150°–160° in sealed tubes with alcoholic potash. It is a colourless liquid, having a pungent alliaceous odour, sp. gr. 0·71 at 13°, and boiling at about 80°. Vapour-density 2·8372 (obs. 2·7938). With bromine it behaves like valerylene (v. 981), forming a liquid dibromide, $C^6H^{10}Br^2$, or a crystallisable tetrabromide, $C^6H^{10}Br^4$, according to the proportion of bromine used (Caventou, *Compt. rend.* lix. 449. Reboul a. Truchot, *ibid.* lxv. 73).

HEXYL ALCOHOLS. $C^6H^{14}O = C^6H^{13}(OH)$.—There may be three *primary hexyl alcohols*, viz.,



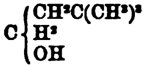
$$\mathrm{C}\left\{\begin{array}{l}\mathrm{CH^2CH^2CH^2CH^2CH^3}\\ \mathrm{H^2}\\ \mathrm{OH}\end{array}\right.$$

Amyl carbinol.



$$\mathrm{C}\left\{\begin{array}{l}\mathrm{CH^2CH^2CH(CH^3)^2}\\ \mathrm{H^2}\\ \mathrm{OH}\end{array}\right.$$

β Amyl carbinol.

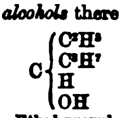


$$\mathrm{C}\left\{\begin{array}{l}\mathrm{CH^2C(CH^3)^3}\\ \mathrm{H^2}\\ \mathrm{OH}\end{array}\right.$$

γ Amyl carbinol.

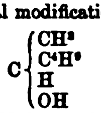
The hexyl alcohol of fermentation (boiling at 148°–154°) discovered by Faget is probably the second of these, being the homologue of ordinary amyl alcohol. The hexyl alcohol obtained by Pelouze a. Cahours (iii. 152) from the hexane of American petroleum boils at 150°, and is probably the first modification. A primary hexyl alcohol, also boiling at 150°, has been obtained by Rossi (*Ann. Ch. Pharm.* cxxxiii. 178), by the action of sodium-amalgam on caproic aldehyde, $C^6H^{12}O$ (produced by distilling calcium caproate with calcium formate). A hexyl alcohol, perhaps also primary, is formed, according to Béchamp, in small quantity by the fermentation of ethyl alcohol in contact with chalk of Sens and syntonin (see FERMENTATION, p. 614): $3C^2H^6O = 2H^2O + C^6H^{14}O$.

Of *secondary hexyl alcohols* there are two principal modifications, viz.,



$$\mathrm{C}\left\{\begin{array}{l}\mathrm{C^2H^5}\\ \mathrm{C^3H^7}\\ \mathrm{H}\\ \mathrm{OH}\end{array}\right.$$

Ethyl-propyl carbinol



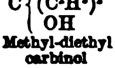
$$\mathrm{C}\left\{\begin{array}{l}\mathrm{CH^3}\\ \mathrm{C^4H^9}\\ \mathrm{H}\\ \mathrm{OH}\end{array}\right.$$

Methyl-butyl carbinol,

the first being further susceptible of two modifications accordingly as the radicle C^3H^7 consists of propyl or isopropyl, and the second of three similar modifications accordingly as the radicle C^4H^9 consists of butyl, $(CH^2)^3CH^3$, or of β-butyl, $CH^2CH(CH^3)^2$, or γ-butyl, $C(CH^3)^3$.

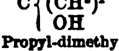
Only two distinct secondary alcohols have, however, been obtained—namely, that which Wanklyn a. Erlenmeyer prepared by treating the hexyl iodide produced by the action of hydriodic acid on mannite with water and silver iodide (iii. 152); and that obtained in like manner by Wurtz from the hexyl iodide resulting from the action of hydriodic acid on the hexylene occurring amongst the products of the distillation of amyl alcohol with zinc chloride (p. 699). The first of these alcohols boils at 137°, the second between 120° and 130°; but the difference of their structure has not been exactly made out. That obtained from mannite yields, by oxidation, a ketone consisting either of methyl-valeryl or methyl-butyl ketone, $\mathrm{CO}\left\{\begin{array}{l}\mathrm{CH^3}\\ \mathrm{C^4H^9}\end{array}\right.$, or of ethyl-butyryl or ethyl-propyl ketone, $\mathrm{CO}\left\{\begin{array}{l}\mathrm{C^2H^5}\\ \mathrm{C^3H^7}\end{array}\right.$; the oxidation-products of Wurtz's alcohol have not been studied.

Of *tertiary hexyl alcohols* there are two principal modifications, viz.,



$$\mathrm{C}\left\{\begin{array}{l}\mathrm{CH^3}\\ \mathrm{(C^2H^5)^2}\\ \mathrm{OH}\end{array}\right.$$

Methyl-diethyl carbinol



$$\mathrm{C}\left\{\begin{array}{l}\mathrm{C^3H^7}\\ \mathrm{(CH^3)^2}\\ \mathrm{OH}\end{array}\right.$$

Propyl-dimethyl carbinol,

the second being further susceptible of modification accordingly as the radicle C^3H^7 consists of propyl or isopropyl.

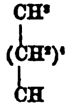
Methyl-diethyl carbinol is obtained by treating acetyl chloride, $COCH^3Cl$, with zinc-ethyl; leaving the product for several days till it has become viscid; then heating it in the water-bath; mixing it with water, whereupon it evolves combustible gases; acidulating with hydrochloric acid; and distilling. The tertiary alcohol then passes over, and after being freed from an admixed ketone by agitation with sodium bisulphite, may be purified by distillation over ignited potassium carbonate. *Propyl-dimethyl carbinol* is prepared in the same manner with butyryl chloride, COC^3H^7Cl, and zinc-methyl.

The tertiary hexyl alcohols thus obtained are similar in their properties to tertiary butyl alcohol (p. 374). They are rather viscid, lighter than water, and somewhat soluble therein, have an alcoholic and camphorous odour, and do not solidify in a freezing mixture. With phosphorus pentachloride they yield the *tertiary chlorides* $CH^3(C^2H^5)^2.CCl$ and $C^3H^7(CH^3)^2.CCl$, which are liquids having peculiar disagreeable odours, and boiling, with decomposition, the former at 110°, the latter at 100°.

Methyl-diethyl carbinol oxidised with a mixture of 3 pts. potassium dichromate, 1 pt. sulphuric acid, and 2 to 4 pts. water, yields (together with carbon dioxide and a hydrocarbon resembling hexylene) only acetic acid; propyl-dimethyl carbinol yields in like manner acetic and propionic acids.

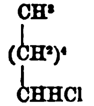
If the product of the action of zinc-ethyl on acetyl chloride be treated with water immediately, instead of being first left to itself for some days, it yields *propyl-methyl ketone*, $CO.C^3H^7.CH^3$, instead of the tertiary alcohol; and the product obtained with butyryl chloride and zinc-methyl, if immediately treated with water, yields *propyl-ethyl ketone*, $CO.C^3H^7.C^2H^5$ (Buttlerow, *Bull. Soc. Chim.* [2] v. 17; *Jahresb.* 1865, p. 461).

HEXYLENE. C^6H^{12}.—This hydrocarbon admits of several isomeric modifications, accordingly as each atom of carbon is united at most with two others, or with three, or with four. (See HYDROCARBONS.) There are two modifications in which neither of the carbon-atoms is associated with more than two others, viz. normal hexylene, $(CH^2)^6$, homologous with ethylene; and hexylidene, $CH^3—(CH^2)^4—CH$, homologous with ethylidene. Normal hexylene does not appear to have been obtained. *Hexylidene* is produced by heating dichlorhexane (hexylidene chloride), $C^6H^{12}Cl^2$, to 90° with sodium, adding the metal by small quantities at first, and applying a stronger heat when the first violent action is over. Hexylidene and unaltered dichlorhexane then pass over together, and may be separated by fractional distillation. Hexylidene boils between 68° and 71°, has a sp. gr. of 0·702 at 0°, unites with bromine with a hissing noise, producing a heavy limpid liquid. Heated with excess of fuming hydrochloric acid to 160°, it is almost wholly converted into hexyl chloride, $C^6H^{13}Cl$, boiling between 125° and 130°, having a sp. gr. of 0·892 at 23°, and identical with that which Pelouze a. Cahours obtained by the action of chlorine on hexane from American petroleum. This chloride heated to 160° with lead acetate is converted into hexyl acetate, $C^6H^{13}.C^2H^3O^2$, without a trace of hexylene; and the acetate treated with potash yields normal hexyl alcohol identical with that obtained by Pelouze a. Cahours (Geibel a. Buff, *Zeitschr. f. Chem.* [2] iv. 179; Buff, *ibid.* 730):



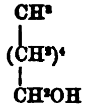
$$\begin{matrix} CH^3 \\ | \\ (CH^2)^4 \\ | \\ CH \end{matrix}$$

Hexylidene.



$$\begin{matrix} CH^3 \\ | \\ (CH^2)^4 \\ | \\ CHHCl \end{matrix}$$

Hexyl chloride.



$$\begin{matrix} CH^3 \\ | \\ (CH^2)^4 \\ | \\ CH^2OH \end{matrix}$$

Hexyl alcohol.

Hexylenes yielding secondary hexyl alcohols are obtained: *α*. Together with other olefines and several paraffins, by distilling amyl alcohol with zinc chloride: B. P. 60°–70° (Wurtz).—*β*. By decomposing secondary hexyl iodide (from mannite) with potash: B. P. 68°–70° (Wanklyn a. Erlenmeyer, iii. 155).—*γ*. By distilling phenose, $(C^6H^6)^{vi}(OH^6)$, or the corresponding trichlorhydrin, $(C^6H^6)^{vi}Cl^3(OH)^3$, with hydriodic acid, whereby hexylene hydriodide or secondary hexyl iodide is obtained:

$$\underset{\text{Phenose}}{C^6H^{12}O^6} + 13HI = C^6H^{12}.HI + 6H^2O + 6I^2$$

$$\underset{\text{Trichlorhydrin}}{C^6H^9Cl^3O^3} + 13HI = C^6H^{12}.HI + 3H^2O + 3HCl + 6I^2;$$

and heating the hydriodide thus obtained with alcoholic potash: hexylene then passes over, boiling at 68°–70° (Carius, *Ann. Ch. Pharm.* cxxxvi. 323).—*δ*. Diallyl dihydriodide, $C^6H^{10}.2HI$, heated with sodium, or better with an alloy of tin and sodium containing a large proportion of the latter, is partly converted into hexylene boiling at 68°–70°, and having a sp. gr. of 0·6937 at 0° (Wurtz, *Jahresb.* 1864, p. 512):

$$C^6H^{10}.H^2I^2 + Na^2 = 2NaI + C^6H^{12}.$$

Hexylene prepared from mannite, or from the hexyl chloride obtained with American petroleum, is converted by careful admixture with bromine into a red liquid not volatile without decomposition, which when heated with silver acetate suspended in ether, and subsequently distilled, yields hexylene diacetate, together with a liquid boiling between 300° and 320°. Hexylene diacetate, $C^6H^{12}.(C^2H^3O^2)^2$, is a colourless oily liquid, insoluble in water, having a sp. gr. of 1·014 at 0°, and boiling between 215° and 220°. By carefully treating it with recently ignited and pulverised potassium hydrate, and distilling the resulting alkaline mass, hexylene alcohol or hexylene glycol, $C^6H^{14}O^2 = C^6H^{12}(OH)^2 = \left.\begin{matrix}(C^6H^{12})'' \\ H^2\end{matrix}\right\}O^2$, is obtained as a thick, colourless liquid, miscible in all proportions with water, alcohol, and ether, having a sp. gr. of 0·9669 at 0°, and boiling at about 207°; that is to say, a few degrees lower than the isomeric compound diallyl dihydrate, $C^6H^{10}.2H^2O$ (p. 94), and 20° to 25° higher than amylene glycol.

Hexylene glycol dissolves completely in very strong hydrochloric acid, forming a liquid which gradually turns brown, and from which, especially when heated, there separates a black liquid boiling between 100° and 250°, but not containing hexylene dichloride. The hydrochloric acid solution distilled with potash yields **hexylene oxide**, $C^6H^{12}O$, boiling at 115°. Hexylene glycol heated to 100° with concentrated hydriodic acid yields a brown solution, from which, after neutralisation with potash, **hexylene monohydriodide** or **secondary hexyl iodide**, $C^6H^{12}.HI$ or $C^6H^{13}I$ (boiling between 165° and 170°), is obtained by distillation:

$$C^6H^{12}(OH)^2 + 3HI = C^6H^{13}I + 2H^2O + I^2.$$

Diallyl dihydrate, $(C^6H^{10})^{iv}\left\{\begin{matrix}H^2\\(OH)^2\end{matrix}\right.$ (p. 94), isomeric with hexylene glycol, is converted by similar treatment with hydriodic acid into diallyl dihydriodide, $C^6H^{10}\left\{\begin{matrix}H^2\\I^2\end{matrix}\right.$. Hexylene monohydriodide treated with dry silver benzoate immediately yields a certain quantity of hexylene (Wurtz, *Ann. Ch. Phys.* [4] iii. 129; *Bull. Soc. Chim.* [2] ii. 161; *Jahresb.* 1861, p. 515).

HIPPURIC ACID, $C^9H^9NO^3$, has the composition of benzamidoglycollic acid, $C^2H^4(C^7H^5O)NO^2$, and is isomeric with acetamidobenzoic or acetoxybenzamic acid, $C^7H^6(C^2H^3O)NO^2$ (ii. 699; iv. 291). It is formed in small quantity by the action of benzamide on chloracetic acid at 150°–160° (Jazukowitsch, *Bull. Soc. Chim.* [2] viii. 361):

$$C^2H^3ClO^2 + (C^7H^5O)H^2N = HCl + C^2H^4(C^7H^5O)NO^2.$$

According to Schulzen a. Naunyn (*Zeitschr. f. Chem.* [2] iv. 29), hippuric acid is found in the urine in considerable quantity after 2 or 3 grms. of toluene have been swallowed. According to Graebe a. Schultzen (*ibid.* iii. 417), cinnamic and mandelic acids, after passing through the organism, appear in the urine as hippuric acid; chlorobenzoic acid as chlorohippuric acid.

A dilute solution of sodium hippurate mixed with a nearly neutral solution of ferric chloride yields a cream-coloured precipitate of **ferric hippurate** containing $Fe^2O^3.2C^{18}H^{16}N^2O^5$, the acid liquid filtered therefrom containing free hippuric acid. The precipitate is not quite insoluble in water, especially in presence of free hippuric acid, and moderately soluble in excess of ferric chloride. On heating the recently precipitated and still moist salt just mentioned, hippuric acid separates, and a more basic salt is formed containing $2F^2O^3.3C^{18}H^{16}N^2O^5$. This latter is also sometimes produced, together with the former, on mixing very concentrated solutions of sodium hippurate and ferric chloride (Salkowski, *Zeitschr. f. Chem.* [2] iv. 313).

When *sodium-amalgam* is gradually added to a boiling aqueous solution of hippuric acid acidulated with hydrochloric acid, glycocine is formed, together with benzyl alcohol, a white crystalline compound, $C^{14}H^{14}O^2$ (identical with that which is obtained in like manner from benzoic acid, p. 307), and a gummy nitrogenous acid apparently related to hippuric acid in the same manner as hydrobenzoic to benzoic acid (M. Herrmann, *Ann. Ch. Pharm.* cxxxiii. 335). In alkaline solution, on the other hand, hippuric acid is converted by sodium-amalgam, first into hydrobenzuric acid, and by further action into hydrobenzyluric acid and glycocine (Otto, p. 703):

$$\underset{\text{Hippuric acid.}}{2C^9H^9NO^3} + 3H^2 = \underset{\text{Hydrobenzuric acid.}}{C^{18}H^{24}N^2O^6}$$

and

$$\underset{\text{Hydrobenzuric acid.}}{C^{18}H^{24}N^2O^6} + H^2 = \underset{\text{Hydroxybenzurillic acid.}}{C^{16}H^{21}NO^4} + \underset{\text{Glycocine.}}{C^2H^5NO^2}$$

Bromhippuric acid, $C^9H^8BrNO^3$, is obtained, by treating a boiling alcoholic solution of hippuric acid with bromine, adding water, and evaporating to one half, as a crystalline deposit made up of small needles. It dissolves in hot water, alcohol, and ether, much more easily than in the same liquids when cold; gives off bromine on exposure to moist air; and when heated with lime, gives off first benzoic acid and then a violet oil. The strongly acid solution is not precipitated by calcium, barium, or copper salts. The potassium and sodium salts are not crystallisable. The calcium salt, $(C^9H^7BrNO^3)^2Ca$, forms slender needles easily soluble in hot water (J. Maier, *Sill. Am. J.* [2] xxxix. 208).

Diazohippuric acid, $C^9H^7N^3O^3$, is obtained as a nitrate by the prolonged action of nitrous acid on amidohippuric acid (iii. 160):

$$C^9H^{10}N^2O^3 + NHO^2 = C^9H^7N^3O^3 + 2H^2O.$$

The nitrate $C^9H^7N^3O^3.NHO^3$, which is explosive, crystallises in white prisms, and dissolves easily in water. The aurochloride $C^9H^7N^3O^3.HCl.AuCl^3$ and the platinochloride are crystallisable (Griess, *Jahresb.* 1862, p. 260).

Iodhippuric acid, $C^9H^8INO^3$, is produced by the action of aqueous hydriodic acid on sulphate of diazohippuric acid, and separates in coloured crystalline masses, which may be purified by solution in ammonia, decolorisation with animal charcoal, and precipitation with hydrochloric acid. It forms laminæ resembling naphthalene, easily soluble in cold alcohol and ether, moderately soluble in hot water, nearly insoluble in cold water. Its ammonium salt forms a white precipitate with silver nitrate (Griess, *Zeitschr. f. Chem.* [2] iv. 725). Another modification of this acid is obtained, like the brominated acid, by treating a boiling alcoholic solution of hippuric acid with iodine. It forms white needles which react like the brominated acid. All its salts are soluble in water excepting the silver salt (Maier). Griess regards the iodated acid obtained from diazohippuric acid as $C^2H^4(C^7H^4IO)NO^2$, and Maier's acid as $C^2H^3I(C^7H^5O)NO^2$. The iodine of the former is as difficult to replace as that of iodobenzoic acid.

Oxyhippuric acid, $C^9H^9NO^4$, is produced by heating the aqueous solution of diazohippuric sulphate to the boiling point, neutralising with ammonia as soon as the evolution of nitrogen ceases, evaporating at 100°, and precipitating with hydrochloric acid. It crystallises in colourless needles, easily soluble in hot water, alcohol, and ether, sparingly soluble in cold water. The aqueous solution is decomposed by nitric acid (Griess, *loc. cit.*).

HOPS. The bitter principle of hops (lupulite) may be obtained in the crystalline state as follows: Fresh hops are exhausted with four times their weight of ether; the blackish residue left on evaporating the ethereal solution is treated with cold alcohol of 90 p. c.; the liquid filtered from the undissolved myricin is freed from alcohol by distillation; and the residue is redissolved in ether. The ethereal solution is agitated, first with strong potash-ley (till the latter is no longer coloured yellow), then with pure water, which dissolves out the bitter principle in combination with potash; the aqueous solution is precipitated with cupric sulphate; and the blue precipitate is washed with a little ether, then dissolved in more ether, and decomposed by hydrogen sulphide. The solution, filtered from the copper sulphide and evaporated to a syrup in a stream of carbon dioxide, gradually yields the hop-bitter as a crystalline mass, which may be freed from the brown mother-liquor by repeatedly moistening it with nitrobenzol on a plate of gypsum. The pure white crystals thus obtained become soft and yellow on exposure to the air; and on recrystallising them from ether, large very brittle rhombic prisms are obtained, covered with a layer of the same substance in the amorphous state. The bitter principle is insoluble in water, but very soluble in alcohol, ether, chloroform, carbon bisulphide, benzol, and oil of turpentine; the alcoholic solution diluted with water has a pure and pleasant bitter taste and a distinct acid reaction. The potash-ley which has been shaken up with the ethereal solution in the process above described contains, besides resin, a second body, which crystallises in white needles melting above 110°, and likewise unites with cupric oxide (Lermer, *Dingl. pol. J.* clxxix. 54).

According to Leuchs (*J. pr. Chem.* ci. 137), the aqueous infusion of hops loses its bitter taste by the action of reducing agents, such as sulphurous acid, aldehyde, and formic acid.

For analyses of the ash of hops, see Lermer (*Jahresb.* 1864, p. 609), Wheeler (*J. pr. Chem.* xciv. 385; *Jahresb.* 1865, p. 636).

HORNBLENDE. For analyses of this mineral, see *Jahresb.* 1862, p. 725; 1864, pp. 836, 837; 1866, 926;—of hornblende rock: *ibid.* 1867, pp. 1014, 1017, 1026.

HYÆNIC ACID. $C^{25}H^{50}O^2$ (Carius, *Ann. Ch. Pharm.* cxxxix. 168).—The anal glandular pouches of the striped hyæna contain a pale yellow buttery mass smelling slightly like musk, and consisting of the glyceride of this acid, together with palmitic and oleic acids. The separation and purification of the acid, which is present in small quantity only, depend upon its comparatively slight solubility in alcohol, and on the fact that it is precipitated by lead acetate from a hot alcoholic solution slightly acidulated with acetic acid, sooner than palmitic acid, while the oleic acid remains entirely in solution.

Hyænic acid resembles cerotic acid more than any other acid of the series $C^nH^{2n}O^2$; it is but slightly soluble in cold absolute alcohol, and separates from solution in boiling alcohol in granules appearing under the microscope to consist of groups of very slender mostly curved needles; in ether it is very slightly soluble. When heated it assumes a soft waxy consistence long before fusion, which takes place at 77°–78°; at 75° it again becomes waxy, and when cooled to the ordinary temperature, hard and friable. The acid thus solidified exhibits under the microscope the same forms as the acid crystallised from alcohol. The alcoholic solution has an acid reaction. The salts, which are insoluble in water, are not decomposed by acetic acid; the potassium and sodium salts form clear solutions only with a very small quantity of warm water, an acid salt being precipitated even on slight dilution. The insoluble hyænates are also converted into acid salts by treatment with a large quantity of water. The *calcium salt* $(C^{25}H^{49}O^2)^2Ca$ is a white crystalline powder, melting at 90°, slightly soluble in hot alcohol. The *lead salt* $(C^{25}H^{49}O^2)^2Pb$ is a white very bulky precipitate, likewise very sparingly soluble in hot alcohol. Whether the hyænic acid is a constituent of the fat of the hyæna in general, or peculiar to the secretion above mentioned, is a question not yet decided.

HYALOPHANE. For analyses of this mineral, see *Jahresb.* 1866, p. 928; 1867, p. 982.

HYDANTOÏC ACID, GLYCOLURIC ACID, or **OXACETYL-UREA.** $C^3H^6N^2O^3 = COH^3(C^2H^3O^2)N^2$.—An acid containing the elements of hydantoïn *plus* H^2O; produced: 1. By the action of potash or baryta-water on hydantoïn (Baeyer, iii. 177).—2. Together with urea, by boiling glycoluril with baryta-water (Rheineck, v. 960):

$$C^4H^6N^4O^2 + 2H^2O = C^3H^6N^2O^3 + COH^4N^2.$$

3. By heating bromacetyl-urea with aqueous ammonia (Baeyer, *Jahresb.* 1864, p. 636):

$$COH^3(C^2H^2BrO)N^2 + NH^3 + H^2O = NH^4Br + COH^3[C^2H^2(OH)O]N^2.$$

4. By heating glycocine with a slight excess of urea (Heintz, *ibid.* 1865, p. 360):

$$C^2H^5NO^2 + COH^4N^2 = NH^3 + COH^3(C^2H^3O^2)N^2.$$

Hydantoïc acid obtained by decomposing its barium salt with sulphuric acid crystallises in large, transparent, colourless, mostly unsymmetrically developed monoclinic prisms exhibiting the combination $\infty P \,.\, \pm P \,.\, (2P\infty) \,.\, oP$. Ratio of clinod. to orthod. to principal axis = 0·662 : 1 : 1·535. Acute angle of axes = 81° 0′. Cleavage perfect parallel to oP. All the hydantoates, even the silver salt, are easily soluble in water, and only some of them crystallise, the rest drying up to amorphous masses. The *potassium salt* $C^3H^5N^2O^3K$, evaporated over sulphuric acid, forms microscopic six-sided tables and rhombohedrons; the *sodium salt* $C^3H^5N^2O^3Na + H^2O$, extremely soluble silky needles, which do not give off water at 133°; the *ammonium salt* $C^3H^5N^2O^3(NH^4) + H^2O$, large crystals, developed like augite at one end only, and becoming opaque from loss of ammonia. The *silver salt* crystallises in small indistinct laminæ, which blacken on exposure to light. The *lead salt* $(C^3H^5N^2O^3)^2Pb + 3H^2O$ crystallises in nodular groups of needles very soluble in water, insoluble in alcohol of 90 p. c., becoming anhydrous at 120° (Herzog, *Ann. Ch. Pharm.* cxxxvi. 276).

HYDANTOÏN, $C^3H^4N^2O^2$, or *Glycolyl-urea*, $CH^2(C^2H^2O)''N^2O$.—Produced: 1. Together with urea, by the action of hydriodic acid on allantoïn.—2. Together with a small quantity of allanturic acid, by the action of hydriodic acid upon alloxanic acid (iii. 177).—3. By heating bromacetyl-urea for several hours to 100° with alcoholic ammonia:

$$CH^3(C^2H^2BrO)N^2O + NH^3 = NH^4Br + CH^2(C^2H^2O)''N^2O.$$

On evaporating the liquor to dryness, washing the residue with a little cold water, boiling it with water and lead hydrate, and removing the lead from the filtrate, the hydantoïn separates in colourless spicular crystals. It is neutral, has a sweet taste, dissolves easily in hot water, melts at 206° to a colourless liquid, which solidifies to a crystalline mass at 157° (Baeyer, *Jahresb.* 1864, p. 637).

Ethyl-hydantoïn. $C^3H^3(C^2H^5)N^2O^2$.—Produced, together with another body sparingly soluble in alcohol, by melting ethyl-glycocine with urea:

$$C^2H^4(C^2H^5)NO^2 + COH^4N^2 = C^3H^3(C^2H^5)N^2O^2 + NH^3 + H^2O.$$

It crystallises from water, or from ether-alcohol, in large well-defined rhombic prisms of 76° 50′, which appear tabular from truncation of the acute prismatic edges (at an angle of 128° 25′); dissolves very easily in water and in alcohol, somewhat less easily in ether; reacts neutral, and does not unite either with bases or with acids. It melts at the heat of the water-bath, and solidifies again but slowly; by continued heating it sublimes as a crystalline deposit (Heintz, *Ann. Ch. Pharm.* cxxxiii. 65; *Jahresb.* 1865, p. 359).

the products of the action of nascent hydrogen on sulphocyanic acid: $SCNH + 2H^2 = NH^3 + CH^2S$ (Hofmann, *Zeitschr. f. Chem.* [2] iv. 689).

FORMOBENZOIC ACID. Syn. with MANDELIC ACID (iii. 799).

FRANGULIC ACID and **FRANGULIN.** Frangulin, the yellow colouring matter of the bark of the berry-bearing alder (*Rhamnus Frangula*), has lately been examined by A. Faust (*Zeitschr. f. Chem.* [2] v. 17), who finds that in the pure state, as prepared by Casselmann's process (ii. 706), it has the composition $C^{20}H^{20}O^{10}$, and that it is a glucoside, being resolved by acids into sugar and frangulic acid:

$$C^{20}H^{20}O^{10} + H^2O = C^6H^{12}O^6 + C^{14}H^{10}O^5.$$

Frangulic acid, $C^{14}H^{10}O^5 + H^2O$, may also be prepared directly from the bark by boiling it with water containing soda instead of ammonia, as in the preparation of frangulin. It is an orange-yellow, loosely coherent, crystalline mass, appearing under the microscope to be composed of long prisms. It melts between 246° and 248°, and gives off its water of crystallisation at 120°; dissolves slightly in water, chloroform, and benzol, easily in alcohol and ethers. Alkalis dissolve it, forming solutions of a fine red colour, from which acids precipitate it unaltered. From its slightly ammoniacal solution, it is precipitated by alkaline earths and by many metallic salts. It dissolves in fuming nitric acid, and the solution when diluted and evaporated, leaves a red mass, probably identical with the nitrofrangulic acid which Casselmann obtained, together with oxalic acid, by the action of fuming nitric acid upon frangulin. *Dibromo-frangulic acid*, $C^{14}H^8Br^2O^5$, is precipitated on mixing an alcoholic solution of frangulic acid with excess of bromine. It is a light-red crystalline mass composed of short slender microscopic needles, sparingly soluble in cold alcohol.

Difrangulic acid, $C^{28}H^{18}O^9 = 2C^{14}H^{10}O^5 - H^2O$, is formed in small quantity in the preparation of frangulic acid from the bark of *Rhamnus Frangula* by boiling with water containing soda, and may be separated from the lead precipitates obtained in the course of the preparation. It is very much like frangulic acid, but has a darker colour; crystallises with 2 mol. water, which are given off at 120°; melts at 248°–250°, that is to say nearly at the same temperature as frangulic acid. This coincidence of melting point appears to be due to the circumstance that frangulic acid, at or a little below its melting point, gives off water and is converted into difrangulic acid.

FRANKLINITE. From an analysis by v. Kobell (*Jahresb.* 1866, p. 922), and a new analysis by Rammelsberg (*ibid.* 1867, p. 979), this mineral appears to have the general formula of the spinels, $MO.M^2O^3$. The mean of Rammelsberg's analyses gave 66·05 p. c. Fe^2O^3, 12·23 Mn^2O^3, and 21·88 ZnO, agreeing with the formula $(\frac{2}{3}MnO.\frac{1}{3}ZnO).Fe^2O^3$.

FRAXIN or **PAVIIN.** From a renewed examination of this substance, obtained from horse-chestnut bark, Rochleder (*J. pr. Chem.* xc. 433; *Jahresb.* 1863, p. 588) concludes that it has the composition $2C^{16}H^{18}O^{10}.H^2O$, and that when heated in a stream of carbon dioxide to 150° (more quickly at 200°) it gives off its water, and then contains $C^{16}H^{18}O^{10}$. After crystallisation from hot alcohol, it is pure white, and gives off its water at 110°–113°. Its decomposition into fraxetin and glucose is represented by the equation:

$$\underset{\text{Fraxin.}}{C^{16}H^{18}O^{10}} + H^2O = \underset{\text{Fraxetin.}}{C^{10}H^8O^5} + \underset{\text{Glucose.}}{C^6H^{12}O^6}$$

FRAXINUS. The leaves of the ash-tree (*Fraxinus excelsior*) contain, according to W. Gintl (*Zeitschr. f. Chem.* [2] iv. 731; v. 377), fat, pectin, a resinous body, optically inactive malic acid (partly free, partly as calcium salt), inosite, mannite, dextroglucose, and a gummy substance not yet examined.

FRUIT. A. Dupré (*Chem. Soc. J.* [2] v. 378) has examined the variations in the proportions of acid and sugar which take place in the ripening of grapes. He finds that a considerable increase in the quantity of sugar is not attended with any essential alteration in the amount of acid: whence it seems to follow that the sugar is not formed from the acid, but that the acid determines the formation of sugar from some other constituents of the fruit.

Sestini (*Bull. Soc. Chim.* [2] vii. 236) has determined the quantities of water, sugar (glucose), and acid in various dried fruits. The numbers in the column headed 'Acid' indicate the volume in cub. cent. of a normal alkaline solution (containing 20 grams soda in a litre) which is neutralised by 100 grams of the fruits.

When recently prepared, it is an inodorous yellowish oil, soluble in ether, alcohol, and alkalis, but insoluble in water; but when exposed to the air, either in the free state or in alkaline solution, it takes up oxygen and is gradually converted into hydroxybenzyluric acid (*q.v.*). Boiled with alkalis out of contact with the air, it is resolved into glycocine, benzyl alcohol, and hydrobenzoic acid:

$$C^{16}H^{21}NO^4 + H^2O = C^2H^5NO^2 + C^7H^8O + C^7H^{10}O^2.$$

HYDROCAFFEIC ACID. $C^9H^{10}O^4$ (Hlasiwetz, *Ann. Ch. Pharm.* cxlii. 353).—Produced by heating caffeic acid with water and sodium-amalgam in a flask provided with a condenser, acidulating the liquid with dilute sulphuric acid without opening the flask more than necessary, and agitating with ether. The aqueous solution of the syrupy residue left on evaporating the ethereal extract, gradually yields colourless rhombohedral crystals of hydrocaffeic acid. It has a slightly acid taste; easily reduces cupric oxide in alkaline solution, also silver nitrate; forms with lead acetate a white precipitate, and with ferric chloride a deep green solution, changing to dark cherry-red on addition of sodium carbonate. The metallic hydrocaffeates are gummy, or when thrown down by alcohol, white precipitates, whose solutions are coloured dark blue by ferric chloride, green by an excess of the latter. The *calcium salt* contains $(C^9H^9O^4)^2Ca$, the *barium salt* $(C^9H^9O^4)^2Ba$; the *lead salt* $(C^9H^7O^4)^2Pb^3$. The acid is therefore tribasic.

In the action of sodium-amalgam on caffeic acid there is also formed a small quantity of a body which is coloured grass-green by a trace of alkali.

HYDROCARBONS. *Classification and Nomenclature.*—The simplest of all hydrocarbons is methane or marsh gas, CH^4, in which the tetrad atom of carbon is united with 4 atoms of hydrogen. The compound thus formed is a saturated molecule, not capable of uniting directly with chlorine, bromine, or other monad element, but only of exchanging a part or the whole of its hydrogen for an equivalent quantity of another monad element. But it may take up any number of dyad elements or radicles, because such a radicle introduced into any group of atoms neutralises one unit of equivalence and introduces another, thereby leaving the combining power or equivalence of the group the same as before. Accordingly the hydrocarbon CH^4 can take up any number of molecules of the bivalent group or radicle CH^2, giving rise to the homologous series of saturated hydrocarbons:

$$CH^4, \quad C^2H^6, \quad C^3H^8, \quad C^4H^{10} \quad . \; . \; . \; . \quad C^nH^{2n+2}.$$

These saturated hydrocarbons may, under various circumstances, be deprived of two atoms or one molecule of hydrogen, producing a new homologous series:

$$CH^2, \quad C^2H^4, \quad C^3H^6, \quad C^4H^8 \quad . \; . \; . \; . \quad C^nH^{2n}.$$

These are unsaturated molecules, having two units of equivalency uncombined, and therefore acting as bivalent radicles.

The first term of this last series cannot give up 2 atoms of hydrogen without being reduced to the atom of carbon; but the remaining terms may give up 2 atoms of hydrogen and thus give rise to the series

$$C^2H^2, \quad C^3H^4, \quad C^4H^6 \quad . \; . \; . \; . \quad C^nH^{2n-2},$$

each term of which is a quadrivalent radicle.

And in like manner, by successive abstraction of H^2, a number of homologous series may be formed, whose general terms are

$$C^nH^{2n+2}, \quad C^nH^{2n}, \quad C^nH^{2n-2}, \quad C^nH^{2n-4}, \text{ \&c.}$$

The individual series, as far as C^6, are given in the following table, together with the names proposed for them by Hofmann (*Proc. Roy. Soc.* xv. 57):

CH^4 Methane.	C^2H^2 Methene.					
C^2H^6 Ethane.	C^2H^4 Ethene.	C^2H^2 Ethine.				
C^3H^8 Propane.	C^3H^6 Propene.	C^3H^4 Propine.	C^3H^2 Propone.			
C^4H^{10} Quartane.	C^4H^8 Quartene.	C^4H^6 Quartine.	C^4H^4 Quartone.	C^4H^2 Quartune.		
C^5H^{12} Quintane.	C^5H^{10} Quintene.	C^5H^8 Quintine.	C^5H^6 Quintone.	C^5H^4 Quintune.	C^5H^2.	
C^6H^{14} Sextane.	C^6H^{12} Sextene.	C^6H^{10} Sextine.	C^6H^8 Sextone.	C^6H^6 Sextune.	C^6H^4	C^6H^2.

These names, proposed by Hofmann in 1863, have not been generally adopted; but a systematic nomenclature for the hydrocarbons, which are the fundamental compounds of organic chemistry, is a great desideratum, and it would not perhaps be easy to devise a better system than that above given. It is true that these names do not carry us beyond the fifth term of each isologous series; but they suffice for most of the hydrocarbons at present known, and it would be easy to extend them by the use of double vowels.

The hydrocarbons of the second homologous series, the olefines C^nH^{2n}, are generally designated by names ending in *ylene*, and these names are perhaps too well established to be altered, but the shorter names without the *yl* are more systematic, and their adoption would be an improvement in our nomenclature.

The formulæ in the preceding table represent hydrocarbons, all of which are capable of existing in the separate state, and many of which have been actually obtained. They are all derived from saturated molecules, C^nH^{2n+2}, by abstraction of one or more *pairs* of hydrogen-atoms.

But a saturated hydrocarbon, CH^4 for example, may give up 1, 2, 3, or any number of hydrogen-atoms in exchange for other elements: thus, marsh gas, CH^4, subjected to the action of chlorine under various circumstances, yields the substitution-products

$$CH^3Cl, \qquad CH^2Cl^2, \qquad CHCl^3, \qquad CCl^4,$$

which may be regarded as compounds of chlorine with the radicles

$$(CH^3)', \qquad (CH^2)'', \qquad (CH^3)''', \qquad C^{iv};$$

and in like manner each hydrocarbon of the series C^nH^{2n+2} may yield a series of radicles of the forms

$$(C^nH^{2n+1})', \qquad (C^nH^{2n})'', \qquad (C^nH^{2n-1})''', \qquad (C^nH^{2n-2})^{iv},$$

each of which has an equivalent value, or combining power, corresponding with the number of hydrogen-atoms abstracted from the original hydrocarbon. Those of even equivalence contain even numbers of hydrogen-atoms, and are identical in composition with those in the table above given; but those of uneven equivalence contain odd numbers of hydrogen-atoms, and are incapable of existing in the separate state, except, perhaps, as double molecules.

These hydrocarbon radicles of uneven equivalence are designated by names ending in *yl*, those of the univalent radicles being formed from methane, ethane, &c., by changing the termination *ane* into *yl*; those of the trivalent radicles by changing the final *e* in the names of the bivalent radicles, methene, &c., into *yl*; and similarly for the rest. The names of the entire series as far as C^3 will therefore be as follows:

CH^4	$(CH^3)'$	$(CH^2)''$	$(CH)'''$				
Methane.	**Methyl.**	**Methene.**	**Methenyl.**				
C^2H^6	$(C^2H^5)'$	$(C^2H^4)''$	$(C^2H^3)'''$	$(C^2H^2)^{iv}$	$(C^2H)^{v}$		
Ethane.	**Ethyl.**	**Ethene.**	**Ethenyl.**	**Ethine.**	**Ethinyl.**		
C^3H^8	$(C^3H^7)'$	$(C^3H^6)''$	$(C^3H^5)'''$	$(C^3H^4)^{iv}$	$(C^3H^3)^{v}$	$(C^3H^2)^{vi}$	$(C^3H)^{vii}$
Propane.	**Propyl.**	**Propene.**	**Propenyl.**	**Propine.**	**Propinyl.**	**Propone.**	**Proponyl.**

General Properties of the Hydrocarbons.

First Series. C^nH^{2n+2}. *Paraffins.*—The name paraffin, signifying chemical indifference (*parum affinis*), has long been applied to a colourless crystalline fatty substance found native in the coal-measures and other bituminous strata, and separable from the least volatile portions of native petroleum, tar, &c. This substance is a hydrocarbon or a mixture of hydrocarbons of the series C^nH^{2n+2} (iv. 344, and *infra*); and the liquid members of the same series are now known commercially as paraffin oils: the name paraffin may therefore be conveniently used as a generic term for the whole series. The names of the first six members, proposed by Hofmann, are contained in the first column of the table above given; the following terms are named *septane*, *octane*, *nonane*, *decane*, *undecane*, *dodecane*, &c.

All the members of the series above the first, CH^4, may be regarded as derived from that compound by replacement of one of the hydrogen-atoms by a univalent hydrocarbon radicle of the series C^nH^{2n+1}; thus:

$$\text{Methane } C\left\{\begin{array}{l} H \\ H \\ H \\ H \end{array}\right.$$

$$\text{Ethane } C^2H^6 = C\left\{\begin{array}{l} CH^3 \\ \ \ H^3 \end{array}\right.$$

$$\text{Propane } C^3H^8 = C\left\{\begin{array}{l} C^2H^5 \\ \ \ \ H^3 \end{array}\right. = C\left\{\begin{array}{l} CH^2CH^3 \\ \ \ H^3 \end{array}\right.$$

$$\text{Quartane } C^4H^{10} = C\left\{\begin{array}{l} C^3H^7 \\ \ \ \ H^3 \end{array}\right. = C\left\{\begin{array}{l} CH^2C^2H^5 \\ \ \ H^3 \end{array}\right. = C\left\{\begin{array}{l} CH^2CH^2CH^3 \\ \ \ H^3 \end{array}\right.$$

&c. &c.

The paraffins are formed: 1. By the simultaneous action of zinc and water on the alcoholic iodides, compounds derived from these same hydrocarbons by the substitution of one atom of iodine for hydrogen.

This reaction, which appears to be applicable to the formation of the whole series of paraffins, is represented by the general equation:

$$2C^nH^{2n+1}I + Zn^2 + 2H^2O = ZnH^2O^2 + ZnI^2 + 2C^nH^{2n+2}.$$

2. By heating the alcoholic iodides with zinc alone. Generally speaking, however, two of these hydrocarbons are obtained together, the first product of the reaction being a paraffin containing twice as many carbon-atoms as the alcoholic iodide employed; and this compound being then partly resolved into the paraffin containing half this number of carbon-atoms and the corresponding olefine, (C^nH^{2n}); thus:

$$\underset{\substack{\text{Ethyl}\\ \text{iodide}}}{2C^2H^5I} + Zn^2 = ZnI^2 + \underset{\text{Quartane,}}{C^4H^{10}}$$

and $$\underset{\text{Quartane.}}{C^4H^{10}} = \underset{\text{Ethene.}}{C^2H^4} + \underset{\text{Ethane.}}{C^2H^6}$$

Generally: $$2C^nH^{2n+1}I + Zn = ZnI^2 + C^{2n}H^{4n+2}$$

and $$C^{2n}H^{4n+2} = C^nH^{2n} + C^nH^{2n+2}.$$

3. By the electrolysis of the fatty acids $C^nH^{2n}O^2$. For example, a solution of potassium acetate divided into two parts by a porous diaphragm, yields pure hydrogen, together with potash, at the negative electrode, and at the positive electrode (if of platinum) a mixture of carbon dioxide and ethane gases:

$$2C^2H^4O^2 = 2CO^2 + C^2H^6 + H^2.$$

The general reaction is

$$2C^nH^{2n}O^2 = 2CO^2 + C^{2n}\ {}^2H^{4n-2} + H^2$$

4. Some of the paraffins are obtained from acids of the series $C^nH^{2n}O^2$ and $C^nH^{2n-2}O^4$, by the action of alkalis, which abstract carbon dioxide from those acids, the hydrocarbon thus eliminated containing one atom of carbon less than the acid from which it is produced:

$$\underset{\text{Acid.}}{C^{n+1}H^{2n+2}O^2} = CO^2 + \underset{\text{Paraffin.}}{C^nH^{2n+2}}$$

$$\underset{\text{Acid.}}{C^{n+2}H^{2n+2}O^4} = 2CO^2 + \underset{\text{Paraffin.}}{C^nH^{2n+2}}$$

In this manner methane (marsh gas) is obtained by heating potassium acetate with excess of potassium hydrate (p. 178):

$$C^2H^3O^2K + KOH = CO^3K^2 + CH^4.$$

Also, sextane and octane, by similar treatment of the potassium salts of suberic acid, $C^8H^{14}O^4$, and sebacic acid, $C^{10}H^{18}O^4$:

$$\underset{\substack{\text{Potassium}\\ \text{suberate.}}}{C^8H^{12}O^4K^2} + 2HKO = 2CO^3K^2 + \underset{\text{Sextane.}}{C^6H^{14}}$$

$$\underset{\substack{\text{Potassium}\\ \text{sebate.}}}{C^{10}H^{16}O^4K^2} + 2HKO = 2CO^3K^2 + \underset{\text{Octane.}}{C^8H^{18}}$$

Generally speaking, however, a further decomposition takes place, resulting in the formation of hydrocarbons containing a smaller proportion of hydrogen than the paraffins.

5. The paraffins may also be produced from the olefines, C^nH^{2n}, by combining the latter with bromine, and heating the resulting compound, $C^nH^{2n}Br^2$, with a mixture of potassium iodide, water, and metallic copper. The bromine-compound is then decomposed, and the hydrocarbon, C^nH^{2n}, is partly reproduced in the free state, partly converted, by the addition of hydrogen, into a paraffin, C^nH^{2n+2}.

6. Several of the paraffins are produced by the dry or destructive distillation of butyrates and acetates.

7. They are also found amongst the products of the dry distillation of coal, especially Boghead and Cannel coal, and they constitute the principal portion of many mineral oils, formed by the gradual decay or decomposition of vegetable matter beneath the earth's surface (iii. 181; iv. 385).

8. Quintyl alcohol, or amyl alcohol, $C^5H^{12}O$, distilled with zinc chloride, yields quintane, C^5H^{12}, and several of its homologues, together with olefines and other hydrocarbons containing still smaller proportions of hydrogen.

9. Methane, CH^4, is produced synthetically by passing a mixture of hydrogen sulphide and vapour of carbon bisulphide over red-hot copper:

$$CS^2 \quad + \quad 2H^2S \quad + \quad Cu^4 \quad = \quad 4CuS \quad + \quad CH^4.$$

Properties and Reactions.—Methane, ethane, propane, and quartane are gaseous at ordinary temperatures; most of the others are liquids, regularly increasing in specific gravity, viscidity, boiling point, and vapour-density, as their molecular weight becomes greater; those containing 20 carbon-atoms or more are crystalline solids. The specific gravities and boiling points of the paraffins obtained from American petroleum are given in the table on p. 181, vol. iii.

The paraffins are especially distinguished by their chemical indifference, exhibiting more completely perhaps than any other class of compounds the characters of perfectly saturated and indifferent molecules, incapable of uniting directly with anything else. With bromine and chlorine they form substitution-products. Methane, CH^4, exposed to the action of chlorine in diffused daylight, forms chloromethane or methyl chloride, CH^3Cl, which by the further action of chlorine in sunshine may be converted into CH^2Cl^2, $CHCl^3$, and CCl^4; and ethane, by a series of processes described under ethyl chloride (ii. 530), may be made to yield the compounds C^2H^5Cl, $C^2H^4Cl^2$, $C^2H^3Cl^3$, $C^2H^2Cl^4$, C^2HCl^5, and C^2Cl^6; similarly with propane, quartane, &c.

Solid paraffin has sometimes been supposed to belong to the olefine series. Analysis will not decide the question, for it is evident that the percentage composition of a hydrocarbon of the series C^nH^{2n+2} or $CH^{2+\frac{2}{n}}$ approaches more nearly to that of an olefine, C^nH^{2n} or CH^2, as the value of *n* becomes greater. The olefines contain 85·7 p. c. carbon and 14·3 hydrogen. In solid paraffin melting at 56°, Gill a. Meusel (*Chem. Soc. J.* [2] vi. 466) found 85·5 carb. and 14·9 hydr., the formula $C^{60}H^{122}$ requiring 85·5 carb. and 14·5 hydr. The same chemists have shown that solid paraffin heated to 50°–100° in hydrochloric acid gas does not unite with it or suffer any alteration of melting point. On exposing it to sunshine in contact with bromine and water, the bromine disappears, half of it being found in the water as hydrobromic acid, showing that a substitution-product has been formed. This accords with the reaction of paraffin with chlorine, as observed some time ago by Bolley and by Brodie (iv. 344). Moreover, paraffin is not attacked by dilute hypochlorous acid, whereas cetene, $C^{16}H^{32}$, combines with that acid, producing rise of temperature. All these reactions show that solid paraffin belongs to the series C^nH^{2n+2}, not to the olefine series C^nH^{2n}, a result which is consistent with its constant occurrence in mineral oils consisting mainly of the liquid homologues of marsh gas, but not containing any well-characterised member of the olefine series.

The paraffins are scarcely attacked by *oxidising agents* at ordinary temperatures; when heated therewith, they are either wholly burnt to water and carbon dioxide, or they yield in addition comparatively small quantities of other oxidation-products, acetic acid, for example, when oxidised by chromic acid. Fuming nitric acid scarcely attacks them in the cold, even after several months, but acts very violently at a gentle heat. Nitric acid of sp. gr. 1·4 yields the same products, but acts less strongly. Sextane and octane (from petroleum) and decane (diamyl) heated with acid of this strength as long as red fumes are evolved, are converted into crystalline succinic acid, together with a nitrogenised yellow oil, and small quantities of fatty acids and nitriles; decane, for example, appears to yield capronitrile, $C^6H^{11}N$, and a mixture of œnanthylic, caproic, and valerianic acids (Schorlemmer, *Proc. Roy. Soc.* xvi. 373). Berthelot (*Jahresb.* 1867, p. 336) found that a few decigrams of sextane required two months' treatment with potassium permanganate to oxidise it completely, yielding a mixture of fatty acids apparently containing caproic acid. Solid paraffin, melting at 56°, boiled for three or four days with sulphuric acid and potassium dichromate, with addition of a little manganese dioxide (which greatly facilitates the reaction), is converted mainly into cerotic acid, $C^{27}H^{54}O^2$, melting at 78°. The same paraffin heated with 5 or 6 vol. nitric acid diluted with 1½ vol. water, yielded a mixture of solid fatty acids, melting after purification at about 76°, and probably therefore containing cerotic acid, also volatile fatty acids, the most abundant of which was œnanthylic acid, while the nitric acid solution contained hydrocyanic acid, succinic acid, and an acid agreeing in composition and melting point with anchoic acid (Gill a. Meusel, *loc. cit.*).

Isomerism in the Paraffin Series.—These hydrocarbons are sometimes regarded as hydrides of the univalent alcohol-radicles C^nH^{2n+1}—methane, for example, as methyl-hydride, $H.CH^3$; ethane as ethyl hydride, $H.C^2H^5$. This view of their constitution is suggested by their formation by the action of water on the zinc-compounds of the same radicles; *e.g.*,

$$Zn(CH^3)^2 + 2H^2O = ZnH^2O^2 + \underset{\text{Methyl hydride}}{2(H.CH^3)};$$

and by the facility with which they give up one atom of hydrogen in exchange for chlorine and bromine, whereas the replacement of the remaining hydrogen-atoms is much more difficult. On the other hand, all these hydrocarbons, except methane, may be regarded as compounds of two atoms or half-molecules of alcohol radicles, C^nH^{2n+1}; thus

$$\underset{\text{Ethane.}}{C^2H^6} = \underset{\text{Ethyl hydride.}}{H.C^2H^5} \text{ or } \underset{\text{Dimethyl.}}{CH^3.CH^3}$$

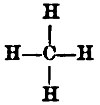
$$\underset{\text{Propane.}}{C^3H^8} = \underset{\text{Propyl hydride.}}{H.C^3H^7} \text{ or } \underset{\text{Methyl-ethyl.}}{CH^3.C^2H^5}$$

$$\underset{\text{Quartane.}}{C^4H^{10}} = \underset{\text{Quartyl hydride.}}{H.C^4H^9} \text{ or } \underset{\text{Diethyl.}}{C^2H^5.C^2H^5} \text{ or } \underset{\text{Methyl-propyl.}}{CH^3.C^3H^7}$$

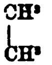
This latter view appears to accord with their formation by the action of zinc on the iodides of the alcohol-radicles, which is similar to that of hydrogen by the action of zinc on hydriodic acid; thus:

$$Zn + 2HI = ZnI^2 + HH.$$
$$Zn + 2C^2H^5I = ZnI^2 + C^2H^5.C^2H^5.$$
$$Zn + CH^3I + C^2H^5I = ZnI^2 + CH^3.C^2H^5.$$

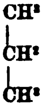
The first three hydrocarbons of the series however, viz. CH^4, C^2H^6, C^3H^8, exhibit exactly the same physical and chemical properties in whatever way they may be prepared; and indeed the constitutional formulæ of these bodies, viz.,



$$\begin{matrix} & H & \\ & | & \\ H— & C & —H \\ & | & \\ & H & \end{matrix}$$



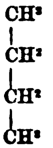
$$\begin{matrix} CH^3 \\ | \\ CH^3 \end{matrix}$$



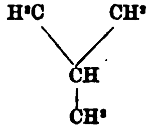
$$\begin{matrix} CH^3 \\ | \\ CH^2 \\ | \\ CH^3 \end{matrix}$$

show that they are not susceptible of isomeric modifications, inasmuch as there is but one way in which the carbon-atoms in either of them can be grouped; in ethane each carbon-atom is directly combined with three hydrogen-atoms and the other carbon-atom; and whether we regard it as ethyl hydride, $\begin{matrix} CH^3 \\ | \\ H—CH^2 \end{matrix}$, or as dimethyl, $H^3C—CH^3$, this arrangement remains the same. In propane, C^3H^8, each carbon-atom is directly combined with at most two other carbon-atoms, and there is no other way in which the atoms can be arranged.

But if we look at the formula of the 4-carbon paraffin, C^4H^{10}, we see that it may be written in either of the following forms:

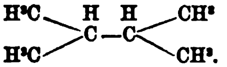


$$\begin{matrix} CH^3 \\ | \\ CH^2 \\ | \\ CH^2 \\ | \\ CH^3 \end{matrix}$$

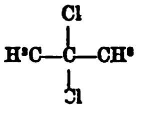


in the first of which neither of the carbon-atoms is directly united with more than two others, whereas in the second one of the carbon-atoms is directly combined with three others. The first may be represented, either as *propyl-methane*, $C\begin{cases}CH^2CH^2CH^3\\H^3\end{cases}$ $= C\begin{cases}CH^2C^2H^5\\H^3\end{cases} = C\begin{cases}C^3H^7\\H^3\end{cases}$, or as *diethyl*, $H^5C^2.C^2H^5$, according to the manner in which we may suppose it to be divided; the second as *trimethyl-methane*, $C\begin{cases}(CH^3)^3\\H\end{cases}$, or *isopropyl methane*, $C\begin{cases}CH(CH^3)^2\\H^3\end{cases}$.

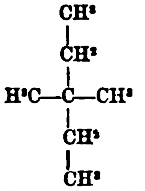
From recent observations by Schorlemmer (*Proc. Roy. Soc.* xvi. 34, 367), it appears that all the paraffins may be divided into four groups, viz.: 1. Those in which each carbon-atom is directly associated with at most two other carbon-atoms.—2. Those in which one carbon-atom is associated with three carbon-atoms, or which contain the group isopropyl once.—3. Those which contain this group twice, such as di-isopropyl, or tetramethyl-ethane, $C^6H^{14} = C^2\begin{cases}H(CH^3)^2\\H(CH^3)^2\end{cases}$, produced by the action of zinc on isopropyl iodide; this compound may be represented by the constitutional formula:



4. Those in which one carbon-atom is associated with four others, as in dimethyl-diethyl-methane, or carbodimethyl-diethyl, $C\begin{cases}(CH^3)^2\\(C^2H^5)^2\end{cases}$, a compound produced by the action of zinc-ethyl on dimethyl-dichloromethane, $C\begin{cases}(CH^3)^2\\Cl^2\end{cases}$, the transformation being effected by the substitution of 2 at. methyl for 2 at. chlorine:



Dimethyl-dichloro-methane.



Dimethyl-diethyl-methane.

The boiling point of a paraffin containing a given number of carbon-atoms is found to be lower in proportion as its structure is more complex. The paraffins of the first group, *e.g.* sextane or hexane (from suberic acid, mannite, and petroleum, iii. 153), and septane or heptane from azelaic acid (p. 696), boil at higher temperatures than their isomerides in either of the other groups. The difference in their boiling points for a difference in composition of CH^2 is 31°. The paraffins of the second group (amyl-hydride 30°, ethyl-butyl 62°, ethyl-amyl 91°, octyl hydride from octyl alcohol 124°) likewise exhibit for a difference of CH^2 a difference in boiling point equal to 31°. The paraffins of the third group (di-isopropyl 58°, dibutyl 58°, butyl-amyl 132°, diamyl 158°) exhibit for each difference of CH^2 a difference in boiling point equal to 25°. Of the fourth group, the only known member is dimethyl-diethyl-methane, which boils at 86° (Schorlemmer).

Second Series. C^nH^{2n}. *Olefines.*—The hydrocarbons of this series are polymeric, as well as homologous, with one another, inasmuch as their formulæ are all exact multiples of that of the lowest, CH^2. The lower members of the series are gaseous at ordinary temperatures, the higher members are solid, and the intermediate compounds liquid. The names and formulæ of the known members of the olefine series are given in the following table, together with their melting and boiling points:

Name	Formula	Melting point	Boiling point
Ethene or Ethylene	C^2H^4	—	—
Propene „ Propylene	C^3H^6	—	−17·8°
Quartene „ Butylene	C^4H^8	—	+3°
Quintene „ Amylene	C^5H^{10}	—	35°
Sextene „ Hexylene	C^6H^{12}	—	68°–70°
Septene „ Heptylene	C^7H^{14}	—	95°
Octene „ Octylene	C^8H^{16}	—	115°–117°
Nonene „ Nonylene	C^9H^{28}	—	140°
Decene „ Paramylene	$C^{10}H^{20}$	—	160°
Sexdecene „ Cetene	$C^{16}H^{32}$	—	275°
Septivigintene „ Cerotene	$C^{27}H^{54}$	57°	(?)
Trigintene „ Melene	$C^{30}H^{60}$	62°	375° (?)

Methene, CH^2, the lowest term of the series, does not appear to be capable of existing in the separate state; but its oxygen analogue, carbon monoxide or carbonyl, CO, is a well-known compound.

Formation of the Olefines.—1. By abstraction of the elements of water from the alcohols of the series $C^nH^{2n+2}O$, under the influence of powerful dehydrating agents, such as oil of vitriol, phosphoric oxide, or zinc chloride; thus:

$$\underset{\text{Ethyl alcohol.}}{C^2H^6O} - \underset{\text{Water.}}{H^2O} = \underset{\text{Ethene.}}{C^2H^4}$$

Quintyl or amyl alcohol, $C^5H^{12}O$, distilled with zinc chloride, yields—besides the corresponding olefine, quintene or amylene, C^5H^{10}—a number of others polymeric with it, also quintane, C^5H^{12}, and its homologues, and hydrocarbons containing a smaller proportion of hydrogen than the olefines.

2. By passing the vapours of the haloïd compounds of the monad radicles C^nH^{2n+1} over lime at a dull red heat; *e.g.*,

$$\underset{\text{Quintyl chloride.}}{2C^5H^{11}Cl} + CaO = CaCl^2 + H^2O + \underset{\text{Quintene.}}{2C^5H^{10}}$$

3. By the decomposition of the paraffins at the moment of their formation by the action of zinc or sodium on the iodides of the monad alcohol-radicles C^nH^{2n+1}.

4. By the action of these same iodides on the sodium-compounds of the same radicles; for example,

$$C^2H^5I + C^2H^5Na = NaI + C^2H^4 + C^2H^6.$$

5. By decomposition of the hydrates of ammonium-bases containing four atoms of a monad alcohol-radicle, these compounds when heated splitting up into a tertiary monamine and an olefine; thus:

$$\underset{\text{Tetrethylammonium hydrate.}}{N(C^2H^5)^4(HO)} = \underset{\text{Triethylamine.}}{N(C^2H^5)^3} + H^2O + \underset{\text{Ethene.}}{C^2H^4}$$

6. Olefines are formed by the decomposition of acetates and butyrates at a red heat, distilling over together with several other products, from which they are separated by combining them with bromine, and heating the resulting bromine-compounds, $C^nH^{2n}Br^2$, to 275° with copper, water, and potassium iodide. In this manner Berthelot has obtained ethene, propene, quartene, and quintene.

7. Several of the olefines may be produced by direct synthesis from other hydrocarbons of simpler constitution.

α. Ethene is formed by the action of nascent hydrogen upon ethine or acetylene:

$$C^2H^2 + H^2 = C^2H^4.$$

β. Propene, C^3H^6, is formed by passing a mixture of methane and carbon monoxide (oxymethene) through a red-hot tube:

$$2CH^4 + CO = H^2O + C^3H^6.$$

Also by the action of methenyl chloride (chloroform) on zinc ethide:

$$2CHCl^3 + 3Zn(C^2H^5)^2 = 3ZnCl^2 + 4C^3H^6 + 2CH^4.$$

γ. **Quintene, or amylene,** C^5H^{10} (or a compound isomeric with it), is formed by the action of zinc ethide on allyl iodide:

$$2C^3H^5I + Zn(C^2H^5)^2 = ZnI^2 + 2C^5H^{10}.$$

δ. **Sextene, or hexylene,** C^6H^{12}, is obtained in combination with hydriodic acid by the action of that acid on mannite:

$$\underset{\text{Mannite}}{C^6H^8(HO)^6} + 11HI = 6H^2O + 5I^2 + \underset{\substack{\text{Sextene}\\ \text{hydriodide};}}{C^6H^{12}.HI}$$

and this hydriodide, heated with potassium hydrate, yields the hydrocarbon:

$$C^6H^{12}.HI + KHO = KI + H^2O + C^6H^{12}.$$

ε. **Quartene, or butylene,** C^4H^8, is obtained by precisely similar reactions from erythrite, $C^4H^6(OH)^4$.

Reactions.—1. The olefines are dyad radicles, uniting with 2 atoms of chlorine, bromine, &c., and with 1 atom of oxygen.

2. The chlorides, bromides, and other haloïd compounds of the olefines, treated with an alcoholic solution of *potash*, give up one atom of hydrogen and one atom of the haloïd element, yielding an olefine in which 1 atom of hydrogen is replaced by chlorine, bromine, &c., together with water and a haloïd salt of potassium; thus:

$$\underset{\substack{\text{Ethene}\\ \text{bromide.}}}{C^2H^4Br^2} + KHO = KBr + H^2O + \underset{\text{Bromethene.}}{C^2H^3Br}$$

The resulting chlorinated, brominated, or iodated compound can, in its turn, take up 2 atoms of chlorine, bromine, or iodine, forming a body which can likewise give up hydrochloric, hydrobromic, or hydriodic acid, under the influence of alcoholic potash; the body thus formed can again take up 2 atoms of chlorine, bromine, or iodine, then give up HCl, HBr, or HI; and thus, by a series of perfectly similar reactions, we at length arrive at bodies consisting of the primitive olefine with all its hydrogen replaced by chlorine, bromine, or iodine, and the dichlorides, dibromides, and di-iodides of these last-mentioned bodies; thus from ethene may be derived the two following series of brominated compounds:

Ethene	C^2H^4	Ethene bromide	$C^2H^4Br^2$	
Bromethene	C^2H^3Br	Bromethene bromide	C^2H^3Br	$.Br^2$
Dibromethene	$C^2H^2Br^2$	Dibromethene bromide	$C^2H^2Br^2$	$.Br^2$
Tribromethene	C^2HBr^3	Tribromethene bromide	C^2HBr^3	$.Br^2$
Tetrabromethene	C^2Br^4	Tetrabromethene bromide	C^2Br^4	$.Br^2$

3. A monochlorinated or monobrominated olefine may give up the atom of chlorine or bromine which it contains, in the form of hydrochloric or hydrobromic acid, whereby it is reduced to a hydrocarbon of the following series: C^nH^{2n-2}. This reaction may take place at 130°–150°, under the influence of alcoholic potash, or, better, of sodium ethylate; thus:

$$\underset{\text{Bromethene.}}{C^2H^3Br} + C^2H^5NaO = NaBr + C^2H^5OH + \underset{\text{Ethine.}}{C^2H^2}$$

4. Ethene bromide and its homologues, treated with silver acetate or potassium acetate, exchange their bromine for an equivalent quantity of the halogenic residue of the acetate, $C^2H^3O^2$, giving rise to diatomic acetic ethers; thus:

$$\underset{\substack{\text{Ethene}\\ \text{bromide}}}{(C^2H^4)''Br^2} + 2C^2H^3O^2K = 2KBr + \underset{\substack{\text{Ethene}\\ \text{diacetate};}}{(C^2H^4)''(C^2H^3O^2)^2}$$

and these ethers, distilled with a caustic alkali, yield diatomic alcohols or glycols; for example:

$$\underset{\substack{\text{Ethene}\\ \text{diacetate.}}}{(C^2H^4)''(C^2H^3O^2)^2} + 2KOH = 2C^2H^3O^2K + \underset{\substack{\text{Ethene}\\ \text{alcohol.}}}{(C^2H^4)''(OH)^2}$$

5. The bromides $C^nH^{2n}Br^2$, heated to 275° with a mixture of potassium iodide, copper, and water, give up their bromine and reproduce the original olefine, together with other hydrocarbons (p. 707).

6. Some olefines, when briskly shaken up with strong sulphuric acid, unite with it, forming acid ethers of sulphuric acid, which contain the monatomic alcoholic radicles corresponding to the olefines; thus:

$$C^2H^4 + SO^4H^2 = SO^4.C^2H^5.H:$$

and these acid ethers distilled with water reproduce sulphuric acid and the monatomic alcohol corresponding to the olefine:

$$\underset{\text{Ethyl-sulphuric acid.}}{SO^4.C^2H^5.H} + H(OH) = SO^4H^2 + \underset{\text{Ethyl alcohol.}}{C^2H^5(OH)}$$

With fuming sulphuric acid (which contains sulphuric oxide in solution) the olefines yield sulpho-acids which are isomeric with the preceding, but are not decomposed by water with formation of an alcohol.

7. Olefines unite with hydrochloric, hydrobromic, and hydriodic acids; and the resulting compounds treated with silver oxide in presence of water give rise to two different reactions which go on simultaneously, one part of the compound exchanging its halogen element for hydroxyl, and thereby producing an alcohol, while another portion gives up hydrochloric, hydrobromic, or hydriodic acid, reproducing the original olefine:

$$2(\underset{\substack{\text{Hexylene}\\\text{hydriodide.}}}{C^6H^{12}.HI}) + Ag^2O + H^2O = 2AgI + 2\underset{\substack{\text{Hexyl}\\\text{alcohol.}}}{C^6H^{14}O}$$

$$2(\underset{\substack{\text{Hexylene}\\\text{hydride.}}}{C^6H^{12}.HI}) + Ag^2O = 2AgI + H^2O + 2\underset{\text{Hexylene.}}{C^6H^{12}}$$

8. **Ethene** agitated with a strongly alkaline solution of potassium permanganate is oxidised to oxalic acid, ($C^2H^4 + O^5 = H^2O + C^2H^2O^4$), which is partly resolved into formic acid and carbon dioxide. **Propene** similarly treated yields malonic acid, ($C^3H^6 + O^5 = H^2O + C^3H^4O^4$), with acetic, oxalic, formic, and carbonic acids as secondary products. **Quintene** or **amylene** appears to yield pyrotartaric acid, $C^5H^8O^4$, together with succinic, malonic, and oxalic acids, and volatile acids of the series $C^nH^{2n}O^2$. In all cases the primary and normal product of the oxidation of an olefine appears to be the corresponding bibasic acid $C^nH^{2n-2}O^4$, the other acids formed at the same time resulting from the decomposition and oxidation of this primary product (Berthelot, *Compt. rend.* lxiv. 85; *Jahresb.* 1867, p. 335).

Many olefines are oxidised by aqueous *chromic acid* to **aldehydes** or **ketones**. Ethene gas is slowly attacked at 120°, and converted into aldehyde C^2H^4O. Propene C^3H^6 is oxidised much more readily and almost at ordinary temperatures, yielding acetone, C^3H^6O. Amylene is violently attacked at ordinary temperatures, with formation of complex products, doubtless derived from a ketone, $C^5H^{10}O$ (Berthelot, *Compt. rend.* lxviii. 334).

9. Saturated aqueous *hydriodic acid* converts olefines even in the cold, and more quickly at 100°, first into the corresponding mono-iodated paraffins, then into the paraffins themselves; *e.g.*,

$$\underset{\text{Ethene}}{C^2H^4} + HI = \underset{\text{Iodethane}}{C^2H^5I}$$

and

$$\underset{\text{Iodethane.}}{C^2H^5I} + HI = \underset{\text{Ethane.}}{C^2H^6} + I^2.$$

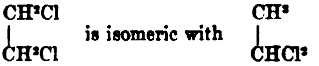
Isomerism in the Olefine Series.—These hydrocarbons may exist in two modifications, one saturated, the other bivalent, according to the manner in which the carbon-atoms are linked together; ethene, C^2H^4, for example, may exhibit the two following modifications:

$$\begin{array}{c} CH^2 \\ \| \\ CH^2 \end{array} \qquad \begin{array}{l} -CH^2 \\ \;\;| \\ -CH^2 \end{array}$$

Saturated. Bivalent.

Ethene in the free state is probably represented by the first of these formulæ, but when it comes in contact with bromine, chlorine, &c., the union of the two carbon-atoms becomes loosened (as in the case of benzene, p. 196), and the molecule assumes the constitution represented by the second formula, in which state it is ready to take up Br^2, Cl^2, O, &c.

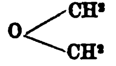
They likewise exhibit in some of their compounds another kind of isomerism, depending upon the relative position of the hydrogen-atoms, which does not affect their equivalent value. Thus the dichlorides of the olefines are isomeric with the monochlorinated chlorides of the alcohol-radicles C^nH^{2n+1}; for example:



$$\begin{array}{l} CH^2Cl \\ | \\ CH^2Cl \end{array} \quad \text{is isomeric with} \quad \begin{array}{l} CH^3 \\ | \\ CHCl^2 \end{array}$$

Ethene dichloride. Monochlorinated ethyl chloride.

Both these compounds, when treated with alcoholic potash, yield the same product, viz. vinyl chloride, C^2H^3Cl, but they differ in boiling point, the former boiling at 85°, the second at 64°. Again, the oxides of the olefines are isomeric with the corresponding aldehydes; *e.g.*,



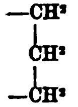
Ethene oxide.

$$\begin{array}{c}CH^3\\ |\\ CHO\end{array}$$

Acetic aldehyde.

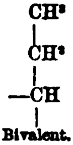
These compounds contain the radicles ethene or ethylene, $CH^2—CH^2$, and ethylidene, $CH^3—CH$, respectively, both of which are bivalent; the latter is not known in the free state.

In the higher terms of the series a greater number of isomeric modifications may occur; thus of the third term, C^3H^6, the following modifications are conceivable:



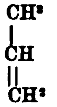
$$\begin{array}{l}—CH^3\\ \quad|\\ \ \ CH^2\\ \quad|\\ —CH^2\end{array}$$

Bivalent.



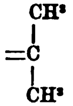
$$\begin{array}{l}\ \ CH^3\\ \quad|\\ \ \ CH^2\\ \quad|\\ —CH\\ \quad|\end{array}$$

Bivalent.



$$\begin{array}{l}CH^3\\ |\\ CH\\ \|\\ CH^2\end{array}$$

Saturated.



$$\begin{array}{l}\ \ CH^3\\ \quad|\\ =C\\ \quad|\\ \ \ CH^3\end{array}$$

Bivalent.

The first of these is normal propylene in combination; the second is propylidene, homologous with ethylidene; the third is perhaps propylene in the free state.

Quartene or butylene, C^4H^8, and its higher homologues may also exhibit modifications similar to those occurring in the paraffins, and depending on the presence of the radicle propyl or isopropyl in the molecule; thus the molecule C^4H^8 may exhibit nine modifications. (See BUTYLENE, p. 375.) In the higher terms still greater variety of constitution is of course possible; indeed, if it be remembered that every olefine is derived from the corresponding paraffin by abstraction of 2 at. hydrogen, and that these two hydrogen-atoms may be taken from the same group CH^3 or CH^2, or one from each of two such groups, it is easy to see that very numerous modifications may arise. Only a small number of these modifications have however been observed in any case. (See HEXYLENE, p. 699.)

Third Series. C^nH^{2n-2}.—Five of these hydrocarbons are known, viz.,

Ethine	or Acetylene,	C^2H^2
Propine	„ Allylene,	C^3H^4
Quartine	„ Crotonylene,	C^4H^6
Quintine	„ Valerylene,	C^5H^8
Sextine	„ Diallyl,	C^6H^{10}

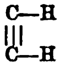
The only general method of preparing these bodies consists in heating the monobrominated derivatives of the olefines, $C^nH^{2n-1}Br$, with sodium ethylate to 130°–150°:

$$C^nH^{2n-1}Br + \underset{\substack{\text{Sodium}\\ \text{ethylate.}}}{C^2H^5NaO} = NaBr + \underset{\text{Ethyl alcohol.}}{C^2H^5(HO)} + C^nH^{2n-2}.$$

Ethine and propine, which are gaseous at ordinary temperatures, are separated from the alcohol vapour with which they are mixed, by passing the gas into an ammoniacal solution of cuprous chloride, whereby an explosive compound is precipitated, containing copper, carbon, hydrogen, and oxygen; and this precipitate, treated with hydrochloric acid, yields the hydrocarbon in the pure state.

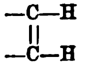
The other hydrocarbons of the series, which are liquid, do not form any precipitate with ammoniacal cuprous chloride; but they may be separated from the excess of alcohol by addition of water, and further purified by distillation.

The hydrocarbons of this series should exhibit three isomeric modifications: saturated, bivalent, and quadrivalent, according to the manner in which the carbon-atoms are united; thus, for the compound C^2H^2:



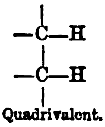
$$\begin{array}{l}C—H\\ |||\\ C—H\end{array}$$

Saturated.



$$\begin{array}{l}—C—H\\ \quad\|\\ —C—H\end{array}$$

Bivalent.



$$\begin{array}{l}\quad|\\ —C—H\\ \quad|\\ —C—H\\ \quad|\end{array}$$

Quadrivalent.

and they do in fact form compounds with 2 and 4 atoms of bromine, chlorine, and figured in vol. v. p. 1030. The air to be dialysed may also be compressed on one side of the septum, and left of the usual tension on the other side.

A large number of experiments made under these several conditions showed that, under given circumstances, the dialytic transfer is accelerated by rise of temperature, and retarded by increased thickness of the membrane.

The quantity of air which passed through a square metre of surface of a caoutchouc balloon 0·114 mm. thick was 16·9 c.c. in a minute; through an equal surface 1 mm. thick, 19·2 c.c. in an hour, or 0·32 mm. per minute; and through an elastic air-cushion (vulcanised caoutchouc between two sheets of cotton), 44·95 c.c. in an hour, or 0·749 c.c. per minute.

The usual proportion of oxygen in air once dialysed by caoutchouc is about 41·6 p.c.: it may be described as air deprived of one-half its usual proportion of nitrogen; but a second and a third dialysis would not increase the amount of oxygen in the same proportion, inasmuch as only half the residual nitrogen would be removed at each operation. The practical problem suggested by the air-dialyser is to attain the means, on a large scale, of reducing to one-half or so the proportion of nitrogen in atmospheric acid. Such air will rekindle a glowing slip of wood, and might be applied to many useful purposes.

On the permeability of caoutchouc for gases, see also Aronstein a. Sirks (*Zeitschr. f. Chem.* [2] ii. 260; *Jahresb.* 1866, p. 52).

2. *Action of Metallic Septa at a Red Heat*:—Deville and Troost in 1863 (*Compt. rend.* lvi. 977; lvii. 894, 965; *Jahresb.* 1863, pp. 23, 26) showed that platinum and iron at a red heat are permeable to hydrogen gas. Graham has confirmed this result and finds that red-hot platinum is very much more permeable to hydrogen than caoutchouc at ordinary temperatures. A square metre of sheet caoutchouc 0·014 mm. thick allowed 127·2 c.c. hydrogen gas to pass through it at 20° in a minute, whereas through an equal surface of platinum tube 1·1 mm. thick at a bright red heat, 489·2 c.c. hydrogen passed in the same time. Oxygen, nitrogen, chlorine, hydrochloric acid, carbon dioxide, carbon monoxide, marsh gas, and ethylene, as well as aqueous vapour, hydrogen sulphide, and ammonia, are not capable of passing through red-hot platinum, the last two perhaps because they are decomposed at that temperature, and only hydrogen passes through the metal. For nitrogen, in presence of hydrogen, platinum appears to be permeable to a slight extent.

This peculiar action of **platinum** may be explained to a certain extent by its property of absorbing hydrogen at a red heat and retaining it for an indefinite length of time at lower temperatures. To demonstrate this property, designated by Graham as '**occlusion**,' the metal to be examined, in the form of wire or fragments, is placed within a porcelain tube glazed inside and out, connected at one end with a Sprengel's vacuum apparatus (as in fig. 823, vol. v. p. 1030), and at the other with a gas-generator or gas-holder. The tube, having been exhausted, is gradually heated to redness, while a copious stream of hydrogen (or other gas) is passed through it, and after prolonged ignition, is left to cool slowly. Finally the unabsorbed gas is expelled by a stream of air; the tube is again exhausted and heated to redness; and the gas thereby expelled from the metal is collected and measured.

Platinum wire (drawn from fused platinum and cleansed by washing with caustic alkali and water) gave off, after an hour's agitation in a vacuum, 0·17 vol. hydrogen to 1 vol. platinum (mean of 4 experiments); platinum-sponge similarly treated yielded 1·48 vol.; old wrought platinum (not originally fused), 3·83 to 5·53 vol. hydrogen; platinum foil at 230° took up 1·45 vol., and between 97° and 100°, in three hours, 0·76 vol. hydrogen. The appearance and lustre of the platinum are not altered by this absorption of hydrogen, but after its expulsion the metal appears white and blistered.

Palladium exhibits a much higher absorbing power for hydrogen. In the form of foil, after recent ignition in a vacuum, it takes up, even at ordinary temperatures, 376 times its volume of hydrogen; at 90° to 97°, 643 vol.; at 245°, 526 vol. The spongy metal obtained by igniting palladious cyanide absorbs 686 times its volume at 200°; foil beaten from the fused metal, only 68 vol.; and an alloy of 5 pts. palladium and 4 pts. silver absorbs 20·5 vol. at a dull red heat. The absorbed hydrogen is given off, partly at ordinary temperatures, quickly at a red heat. In this absorbed and condensed state the hydrogen appears to possess intensified affinities, inasmuch as the palladium which has absorbed it reduces ferric to ferrous salts, ferricyanides to ferrocyanides, and in contact with aqueous chlorine or iodine, forms hydrochloric or hydriodic acid. These properties, viewed in connection with the power which palladium possesses of absorbing perceptible quantities of different liquids, were regarded by Graham as tending to support the assumption that the hydrogen thus absorbed passes into the liquid state. The absorptive power of palladium for hydrogen is related to its permeability by that gas, though the two properties are not exactly proportional

HYDROCARBOSTYROL. $C^9H^9NO = (C^6H^4)''\left\{\begin{matrix}(NH)''\\(C^3H^4O)''\end{matrix}\right.$ (Buchanan a. Glaser, *Zeitschr. f. Chem.* [2] v. 194).—A body produced by reduction of nitrophenyl-propionic acid in the same manner as carbostyrol or carbostyryl from nitrocinnamic acid (i. 802). It has the composition of amidophenyl-propionic acid, $C^9H^{11}NO^2$, *minus* H^2O. To prepare it, nitrophenyl-propionic acid is treated with tin and hydrochloric acid, and the crystals which separate from the diluted and filtered liquid are recrystallised several times from alcohol. It is a very stable substance, melting at 160°, and distilling without decomposition at a higher temperature. In its chemical relations it resembles the amides. It dissolves easily in warm concentrated hydrochloric or hydrobromic acid, apparently forming definite compounds, which, however, decompose spontaneously even in the cold. Potash and soda dissolve it but slowly even at the boiling heat; it is nearly insoluble in water, moderately soluble in alcohol and ether.

HYDROCINNAMIC ACID. See CINNAMIC ACID (p. 468).

HYDROCITRIC ACID. See CITRIC ACID (p. 473).

HYDROCOMENIC ACID, $C^6H^6O^5$, is produced by the action of sodium-amalgam on comenic or bromocomenic acid. It is a yellowish, strongly acid, syrupy liquid forming a white silver salt, $C^6H^4Ag^2O^5$, easily reduced by heat (J. v. Korff, *Ann. Ch. Pharm.* cxxxviii. 191).

HYDROCOUMARIC or **MELILOTIC ACID.** $C^9H^{10}O^3$ (Zwenger a. Bodenbender, *Ann. Ch. Pharm.* cxxvi. 257; Zwenger, *ibid. Suppl.* v. 100; *Jahresb.* 1867, p. 439). This acid occurs, combined with coumarin, in the yellow melilot (*Melilotus officinalis*), forming the compound $C^{18}H^{16}O^5 = C^9H^{10}O^3 . C^9H^6O^2$, which may be called melilo-coumarin. (See COUMARIN, p. 499.) When the aqueous decoction of the plant, evaporated to the consistence of a thin extract, is treated with ether as long as the ether acquires an acid reaction, and the green mass which remains after distilling off the ether is repeatedly boiled with a large quantity of water, well-defined crystals of melilo-coumarin separate on cooling. The solution of these crystals (or the aqueous decoction of the extract above mentioned) is mixed with basic lead acetate, carefully avoiding an excess, which would exert a solvent action; and the precipitate which forms after long standing is collected on a filter, washed first with cold water, then with alcohol and ether to remove free coumarin, and repeatedly boiled with water, as long as the hot filtrate deposits a crystalline precipitate of lead hydrocoumarate. This precipitate decomposed by hydrogen sulphide yields hydrocoumaric acid, which may be purified by repeated precipitation with neutral lead acetate: 100 pounds of the plant yield from 1½ to 2 ounces of the pure acid.

Hydrocoumaric acid may be produced synthetically from coumarin by gradually adding sodium-amalgam to an aqueous solution of that substance containing a little alcohol, each portion of sodium-amalgam being added only after the alkaline reaction produced by the preceding portion has nearly disappeared. By this treatment the coumarin, in the course of a few days, is almost wholly converted into hydrocoumaric acid, which may be precipitated by lead acetate. On boiling the precipitate with water, the greater part, consisting of lead hydrocoumarate, dissolves, while a small quantity of coumarate remains behind, showing that the coumarin, $C^9H^6O^2$, has first been converted, by addition of the elements of water, into coumaric acid, $C^9H^8O^3$, which has then been converted into hydrocoumaric acid by addition of 2 at. hydrogen.

Hydrocoumaric acid dissolves in 20 pts. water at 18°, in less than 1 pt. at 40°, very easily also in alcohol and ether. From a hot-saturated aqueous solution it crystallises, after long standing at ordinary temperatures, in spicular arragonitic crystals an inch long. It melts at 82°; solidifies in the crystalline state on cooling; has a strong acid reaction, a sour astringent taste, an aromatic honey-like odour; decomposes carbonates with facility; and dissolves zinc and iron when heated, with elemination of hydrogen. Its solution in excess of ammonia, when exposed to the air, gradually acquires an indigo-blue colour, becoming reddish when the liquid is heated. On adding the aqueous solution by drops to dilute *ferric chloride*, a bluish coloration is produced, which gradually disappears, with formation of a yellowish precipitate. *Chloride of lime* colours the solution yellow and red when heated. By fusion with *potash*, hydrocoumaric acid is resolved, with evolution of hydrogen, into salicylic and acetic acids:

$$C^9H^{10}O^3 + 2H^2O = C^7H^6O^3 + C^2H^4O^2 + 2H^2.$$

The *metallic hydrocoumarates* are for the most part easily crystallisable; those of the alkali-metals and alkaline earth-metals have a slight alkaline reaction, the ammonium salt and the salts of the heavy metals an acid reaction. The less soluble salts are obtained by precipitation; the more soluble by neutralisation of the corresponding place in the first instance, and that even at very high temperatures a small quantity of hydrogen may be retained by the metal; direct proof of this retention was indeed obtained in one instance by heating a piece of palladium foil in a hydrogen flame and rapidly plunging it into cold water; the hydrogen thus occluded (measured in the cold) amounted to 1·3 times the volume of the metal. Platinum similarly treated took up only 0·06 vol. The velocity of transmission of the gases, which increases rapidly with rise of temperature, is not proportional to the volume taken up by the same metal at lower temperatures. Bar iron takes up a larger quantity of carbon monoxide (4 vol.) than of hydrogen; nevertheless a wrought-iron tube 1·7 mm. thick, after being freed from gases, transmitted through a square metre of surface only 0·284 c.c. carbon monoxide, whereas the hydrogen which passed through the same surface in the same time amounted to 76·5 c.c.* A palladium tube transmitted at 165°, through a square metre of surface, 327 c.c. hydrogen in a minute, at a red heat (melting point of gold) 3992·2 c.c., and of carbon dioxide at the same high temperature only 1·86 c.c. On passing a mixture of equal volumes of hydrogen and carbon dioxide through a small palladium tube, 3 mm. in internal diameter, and 0·3 mm. thick, heated to redness while a vacuum was made around it, 1017·5 c.c. of perfectly pure hydrogen passed through a square metre of its surface in a minute. The rapid diffusion of hydrogen (and partially of carbon monoxide) in palladium, platinum, and iron, at very high temperatures, and their passage through these metals, are regarded by Graham as depending upon a solution of the liquefied gas in the colloïd-metal; in fact, as similar to the passage of gases through a thin membrane of caoutchouc. The solution-affinity of these metals appears, however, to be limited to the two gases just mentioned.

In palladium more or less saturated with hydrogen, Graham assumes the existence of a palladium hydride, the hydrogen alloying itself with the palladium like a metal (see HYDROGEN). The quantity of hydrogen taken up by the palladium, when made to form the negative pole of an electrolytic cell, approximates to the formula PdH^2 (no such hydride can however be formed by the action of sodium hypophosphite on palladium sulphate). The palladium hydride formed by occlusion of hydrogen in palladium wire exhibits the colour and lustre of palladium; its tenacity is but slightly less than that of pure palladium; its electric conductivity is 5·99, that of pure palladium being 8·10 (copper = 100). It is distinctly magnetic, more so than palladium itself. Its density is less than that of pure palladium (*Proc. Roy. Soc.* xvi. 422; xvii. 212, 500; *Chem. Soc. J.* [2] vii. 419).

GLAUCODOTE. A specimen of this mineral from Hakansbö in Sweden, analysed by E. Ludwig (*Jahresb.* 1867, p. 974), gave 19·80 p. c. sulphur, 44·03 arsenic, 19·34 iron, 16·06 cobalt (= 99·23). It has the form of arsenical pyrites, and in respect to its amount of cobalt, is intermediate between the glaucodote of Huasco in Chile (ii. 846), and the less cobaltiferous arsenical pyrites distinguished by Tchermak as danaïte.

GLAUCONITE. Analyses of this mineral from various localities by Haushofer gave, on the average, 49·6 p. c. silica, agreeing approximately with the formula $RO.R^2O^3.3SiO^2 + 3aq.$ (*Jahresb.* 1866, p. 938; 1867, p. 995).

GLUCOSE. See SUGAR.

GLUCOSIDES. Hlasiwetz (*Ann. Ch. Pharm.* cxliii. 290) divides compounds which yield sugar or saccharine substances when treated with acids or alkalis, into the following groups: 1. *Glucosides* yielding by decomposition with dilute mineral acids (or with ferments), glucose and another substance. (*α*) 1 mol. glucose and 1 mol. of the other product; *e.g.* arbutin, helicin, ruberythrin, salicin. (*β*) More than 1. mol. glucose: daphnin, æsculin, jalappin, scammonin, helleborin, turpethin. (*γ*) 1 mol. glucose to 2 mol. of another body: populin, benzohelicin, gratiolin (?), bryonin (?), ononin (?).—2. *Phloroglucides*, which when decomposed by alkalis or strong mineral acids yield phloroglucin: phloretin, quercitrin, maclurin, luteolin, catechin, filicic acid.—3. *Phloroglucosides*; these yield glucose and phloroglucin, the first of which may be separated by dilute acids, the second from the resulting phloroglucide by alkalis: phlorizin, quercitrin, robinin, rutin.—4. *Gummides* yielding glucose as product of transformation: to this division belong perhaps tannic acid and caffeic acid.—5. *Mannides*, yielding a derivative of mannite as a product of decomposition: quinovin, caffetannic acid (?).—6. *Nitrogenous glucosides*: amygdalin, solanin, indicin, chitin.

GLUTAMIC ACID. $C^5H^9NO^4$ (Ritthausen, *J. pr. Chem.* xcix. 454; cvii. 218).—An acid obtained by decomposition of gluten. It may be prepared by boiling the portion of wheat-gluten which is insoluble in alcohol (vegetable fibrin), or better, the portion soluble in alcohol (mucin or mucedin, ii. 873), for 20 to 24 hours with 2½ pts. sulphuric acid and 6 to 7 pts. water, supersaturating with milk of lime, removing the lime with oxalic acid, the excess of the latter by boiling with lead carbonate, and lastly the dissolved lead with hydrogen sulphide. The strongly acid liquid yields by evaporation a crystalline mixture of tyrosine, leucine, and glutamic acid, from which, by treatment with hot water (which leaves the tyrosine undissolved), and then with alcohol of 30 p. c. (which chiefly dissolves the leucine), and recrystallisation from water (with addition of animal charcoal), and from alcohol of 30 p. c., the glutamic acid is obtained pure. The portion of gluten insoluble in alcohol yields only about 1½ p. c. glutamic acid, but mucedin yields more than 30 p. c., with no tyrosine, and only a small quantity of leucine.

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* According to Cailletet (*Compt. rend.* lxvi. 847; *Jahresb.* 1868, p. 137), iron is under certain circumstances permeable to hydrogen at ordinary temperatures.

Glutamic acid is likewise obtained, together with aspartic acid and a non-crystallisable body, by treating conglutin with sulphuric acid. On repeatedly boiling the resulting knobby crystalline masses with alcohol of 50–60 p. c., the greater part of the aspartic acid remains undissolved, and an additional quantity of that acid separates from the hot alcoholic solution, while the glutamic acid remains in the mother-liquors, and may be obtained by distillation and concentration over sulphuric acid, in shining tetrahedral crystals.

Glutamic acid dissolves at 15° in 100 pts. water, 302 pts. alcohol of 30 p. c., and 1,500 pts. alcohol of 80 p. c.; at higher temperatures its solubility in water and in dilute alcohol is much greater. The solutions have a strong acid reaction, an astringent taste, and decompose carbonates, forming soluble salts. From hot-saturated solutions the acid separates in white crystalline crusts composed of shining laminæ, by slow evaporation in crystals having a bright adamantine lustre and the form of distorted rhombic octohedrons with basal end-face. Axes $a : b : c = 0{\cdot}8059 : 1 : 0{\cdot}8521$. They are anhydrous, melt with partial decomposition at 135°–140°, then solidify very slowly to a crystalline mass, which decomposes at a higher temperature, emitting an odour like that of burnt horn. It is dextrogyrate; but when heated with nitrous acid it yields an optically inactive acid homologous with malic acid. The glutamates of the alkali-metals are very soluble, and crystallise with difficulty; those of the alkaline-earth-metals are also very soluble in water and alcohol, and dry up to gummy masses. The *copper salt* separates from aqueous solution in well-defined deep blue crystals, consisting—according to Ritthausen's latest observations—of $C^5H^7NO^4Cu + 2\frac{1}{2}H^2O$; from a very strong solution slightly acidulated with nitric acid, it crystallises in small prisms containing only $2H^2O$, and when precipitated by alcohol, it has the composition $C^5H^7NO^4Cu + 3H^2O$. Lead salts do not precipitate glutamic acid even on addition of ammonia.

GLUTARIC ACID. $C^5H^8O^5$.—An acid homologous with malic acid, produced by the action of nitrous acid on glutamic acid dissolved in dilute nitric acid. It is bibasic. The *calcium salt* $C^5H^6CaO^5 + \frac{1}{2}H^2O$, obtained by neutralisation and precipitation with alcohol, is white, non-crystalline, and flocculent. Decomposed with lead acetate it yields the lead salt in form of a white precipitate, which crystallises from solution in hot water in nodular crystals containing $C^5H^6PbO^5 + \frac{1}{2}H^2O$. In presence of ammonia a basic salt is precipitated. The silver salt is a curdy precipitate, having when dried the composition $C^5H^6Ag^2O^5 + \frac{1}{2}H^2O$. The acid itself crystallises with difficulty from its solution evaporated to a syrup (Ritthausen, *J. pr. Chem.* ciii. 239; *Zeitschr. f. Chem.* [2] iv. 529).

GLUTEN. For a continuation of Ritthausen's investigation of the constituents of gluten (ii. 873), see *J. pr. Chem.* xcix. 462; *Jahresb.* 1864, p. 719.

GLYCERALS. Compounds analogous to the acetals produced by heating glycerin with aldehydes to 170°–200° for 24 to 30 hours:

$$C^3H^8O^3 + \text{Aldehyde} - H^2O = \text{Glyceral}.$$

The following have been obtained:

		B.P.	Sp. gr. at 0°	Vap. density obs.
Acetoglyceral,	$\left.\begin{matrix}C^3H^5\\H\\C^2H^4\end{matrix}\right\}O^3$,	184°–188°	1·081	4·162
Valeroglyceral,	$\left.\begin{matrix}C^3H^5\\H\\C^5H^{10}\end{matrix}\right\}O^3$,	224°–228°	1·027	5·526
Benzoglyceral,	$\left.\begin{matrix}C^3H^5\\H\\C^7H^6\end{matrix}\right\}O$.			

hydrogenium. Assuming that the hydrogen enters into the combination with the density which it would exhibit if solidified in the free state, he calculates, from the observed density of this so-called alloy of palladium and hydrogenium, and of similar alloys containing, in addition, gold, silver, or nickel, that the density of this hypothetically solidified hydrogen varies between the limits 0·711 and 0·7545 : mean, 0·733.

It may, however, be doubted whether the observed modifications of the physical properties of palladium and other metals consequent on the absorption of hydrogen have any very direct bearing on the question of the metallic nature of hydrogen. What indeed is meant by the assertion that hydrogen is a metal? This element, in its chemical relations with chlorine, oxygen, and other chlorous radicles, undoubtedly exhibits striking analogies to the metals, and hence it has been inferred that if liquefied or solidified it would also exhibit the physical characters of a metal. But hydrogen in a state of combination may also be regarded as the first term of the series

$$H \quad CH^3 \quad C^2H^5 \quad C^3H^7 \;.\;.\;.\;.\; C^nH^{2n+1},$$

and in the free state, as the first term of the series

$$H^2 \quad CH^4 \quad C^2H^6 \quad C^3H^8 \;.\;.\;.\;.\; C^nH^{2n+2}.$$

Its chemical analogies to the several terms of the first series (the alcohol-radicles) are well known; and hence we might with equal reason suppose that, if liquefied or solidified, it would resemble the bodies of the second series (the paraffins), exhibiting the appearance of a transparent colourless liquid, or of solid paraffin, and not bearing the slightest resemblance to a metal.

In connection with this subject we may refer to the late ingenious experiments of Seeley (*Chem. News*, June 10, 1870) on the so-called ammoniacal amalgam, from which it appears that this substance when submitted to varying pressure changes its volume like a gas, and is in fact nothing but a homogeneous froth formed by the imprisonment of gas-bubbles between the pores of the mercury. Loew, by shaking together in a well-cooled vessel a mixture of mercury and 1 to 2 p. c. zinc, with an equal bulk of a solution of platinic chloride containing 10 p. c. of the solid salt, has obtained a slimy mass which, when treated with dilute hydrochloric acid, acquires a buttery consistence, and is a compound or mixture of mercury and hydrogen, designated by Loew as *hydrogenium amalgam*, and described as analogous in its properties to Graham's hydrogenised palladium. It is perhaps merely a mixture similar to the ammonium amalgam, and if the molecules of palladium were as free to move as those of the mercury, it would probably also, in absorbing hydrogen, assume the consistence of a metallic froth.

On the spectrum of hydrogen see SPECTRAL ANALYSIS.

On the coloration of the hydrogen flame by small quantities of gaseous and solid bodies, see W. F. Barrett (*Phil. Mag.* [4] xxx. 321; *Jahresb.* 1865, pp. 124, 139).

Reduction of Metallic Salts by Hydrogen.—Pure hydrogen passed for several hours through a solution of nitrate, sulphate, or acetate of *silver*, throws down a slight grey precipitate of metallic silver; impure hydrogen forms a brown or black precipitate, due to the foreign substances present. A solution of *platinic chloride* made as neutral as possible, or a solution of ammonium chloroplatinate, becomes turbid when hydrogen is passed through it, depositing a black, pulverulent, sometimes scaly, metallically lustrous precipitate; by prolonged exposure to the gas the solution becomes colourless and transparent. *Palladium* is precipitated with still greater facility. *Iridium solutions* are scarcely affected; *gold solutions* not at all. Solutions of *mercurous nitrate* and *mercuric chloride* are not affected under the ordinary pressure, but under a pressure of 100 atmospheres metallic mercury is deposited after 24 hours. A solution of *ferric chloride* treated with hydrogen for 48 hours was found to contain a small quantity of ferrous chloride (Brunner, *Pogg. Ann.* cxxii. 153; *Jahresb.* 1865, p. 124). According to Beketoff (*Ann. Ch. Pharm.* cx. 312; *Jahresb.* 1859, p. 66; 1865, p. 13), the reduction of silver from its salts by hydrogen is greatly facilitated by increased pressure. Dilute solutions of cupric nitrate and of lead salts exhibit no trace of metallic precipitation by hydrogen, even under a pressure of 40 atmospheres; but the reduction takes place in presence of platinum, not only under increased pressure, but even under ordinary pressure, if the platinum plate projects above the liquid (the tubes containing the solution and the platinum plate were filled with hydrogen and sealed up). Solutions of silver sulphate similarly treated deposited metallic silver on the platinum; lead solutions were unaffected.

On the temperatures at which different metallic oxides are reduced by hydrogen, see W. Müller (*Zeitschr. f. Chem.* [2] v. 507). Auric chloride is not decomposed by hydrogen at 200°, but above that temperature explosion occurs in consequence of the combination of liberated chlorine with the hydrogen. Platinic chloride begins to be reduced at 85°. The chlorides of silver and lead are not affected; gold sulphide gives off sulphur at 200° (Müller).

HYDROGEN DIOXIDE. H^2O^2.—According to H. Struve (*Zeitschr. f. Chem.* [2] v. 274), this compound occurs frequently in the atmosphere, and may be detected in snow and rain-water, by means of a solution of lead oxide in potash, with addition of a few drops of basic lead acetate, whereby, if hydrogen dioxide is present, a precipitate is formed containing lead dioxide, PbO^2. Houzeau, on the other hand (*ibid.* iv. 375), was not able to detect hydrogen dioxide in snow or rain-water. According to Schönbein (*Jahresb.* 1864, p. 666), hydrogen dioxide may be detected in variable but always small quantity in human urine.

On the formation of hydrogen dioxide in various cases of slow oxidation, as when an amalgam of tin, lead, or bismuth is agitated with water acidulated with sulphuric acid, see Schönbein (*Pogg. Ann.* cvi. 307; cxxii. 445; *Jahresb.* 1859, p. 60; 1861, pp. 94, 96, 97, 156; 1862, p. 42; 1864, p. 121; 1866, p. 101).

To prepare a dilute solution of hydrogen dioxide for lecture experiments, C. Hoffmann (*Ann. Ch. Pharm.* cxxxvi. 188) adds potassium peroxide by small portions to a moderately concentrated and well-cooled solution of silicofluoric or tartaric acid, taking care not to neutralise the acid completely. The potassium peroxide is prepared for the purpose by directing a jet of air on potassium fused in a porcelain crucible.

Reactions.—The reactions of hydrogen dioxide with metals and metallic salts have been studied by Weltzien (*Ann. Ch. Pharm.* cxxxviii. 129; *Chem. News*, xiii. 159; xiv. 1, 15, 39, 50; *Jahresb.* 1866, p. 107). 1. *Metallic iron* in a solution of hydrogen dioxide becomes covered with gas-bubbles and is converted into normal ferric hydrate: $Fe^2 + 3H^2O^2 = Fe^2(OH)^6$.—2. *Aluminium* is acted upon in a similar manner.—3. *Ferrous sulphate* gives a precipitate of a basic ferric salt, $Fe^4SO^9 + 8H^2O$ or $2Fe^2O^3.SO^3 + 8H^2O$, while an acid salt, $Fe^2S^5O^{18}$ or $Fe^2(SO^4)^3.2SO^3$, remains dissolved:

$$6FeSO^4 + 3H^2O^2 + 5H^2O = Fe^4SO^9.8H^2O + Fe^2S^5O^{18}.$$

If the solution of ferrous sulphate be mixed, first with potash, and then with hydrogen dioxide, in excess, the precipitated ferrous hydrate quickly passes into ferric hydrate, corresponding, when dried at 100°, to the formula $Fe^2H^4O^5$ or $Fe^2O^3.2H^2O$. A solution of ferrous sulphate mixed with potassium sulphocyanate turns red on addition of hydrogen dioxide, while ferric hydrate is precipitated:

$$6Fe(CNS)^2 + 3H^2O^2 = 2Fe^2(CNS)^6 + Fe^2H^6O^6.$$

A solution of *ferrous iodide* gives with hydrogen dioxide a precipitate of ferric hydrate, with separation of the whole of the iodine:

$$2FeI^2 + 3H^2O^2 = Fe^2H^6O^6 + 2I^2.$$

Ferric salts are not altered by hydrogen dioxide.—4. *Magnesium* slowly forms an alkaline liquid, which, when evaporated, leaves a white mass perfectly soluble in water, the solution probably containing magnesium hydrate, MgH^2O^2.—5. *Thallium* is converted into thallious and thallic hydrate, according to the equation:

$$2Tl^2 + 4H^2O^2 = 2TlHO + Tl^2H^2O^4 + 2H^2O.$$

On the other hand, thallic hydrate is slowly reduced by hydrogen dioxide to thallious hydrate, with elimination of oxygen, as already observed by Schönbein (*Jahresb.* 1864, p. 171).—6. *Silver nitrate* in ammoniacal solution is reduced by hydrogen dioxide, with brisk evolution of oxygen; probably thus:

$$2(NH^3Ag.NO^3) + H^2O^2 = 2(NH^4.NO^3) + Ag^2O^2$$

and

$$Ag^2O^2 + 2H^2O^2 = Ag^2 + 2H^2O + 2O^2.$$

7. *Potassium iodide* is decomposed by perfectly pure hydrogen dioxide (contrary to the statement of Meissner (*Jahresb.* 1863, p. 144), the liquid becoming alkaline. The reaction takes place by three stages:

$$\begin{aligned}
&(1)\ 2KI + H^2O^2 = K^2O^2 + 2HI.\\
&(2)\ K^2O^2 + H^2O = 2KHO + O.\\
&(3)\ 2HI + O = H^2O + I^2.
\end{aligned}$$

[According to Meissner (*Jahresb.* 1863, p. 144), hydrogen dioxide does not decompose potassium iodide in perfectly neutral solution; according to Houzeau (*ibid.* 1868, p. 146), the decomposition does not take place when the solutions are neutral and very dilute.]

8. *Potassium permanganate* is decomposed by hydrogen dioxide, in the absence of hydrochloric acid, with separation of manganic hydrate, $Mn^2H^2O^4$, and formation of potassium hydrate:

$$2KMnO^4 + 2H^2O^2 = 2KHO + Mn^2H^2O^4 + 3O^2;$$

in presence of hydrochloric acid a manganous salt is formed, as previously shown by Brodie (*Jahresb.* 1861, p. 105):

$$2KMnO^4 + 5H^2O^2 = 2KHO + 2MnO + 4H^2O + 5O^2.$$

9. *Potassium ferrocyanide* in neutral solution is converted into ferricyanide, with formation of potassium hydrate:

$$2K^4FeCy^6 + H^2O^2 = K^6Fe^2Cy^{12} + 2KHO;$$

in presence of hydrochloric acid, not in excess, the reaction is

$$2K^4FeCy^6 + 2HCl + H^2O^2 = K^6Fe^2Cy^{12} + 2KCl + 2H^2O:$$

with excess of hydrochloric acid, hydroferrocyanic acid is separated and further decomposed. On the other hand, ferricyanide is reduced by hydrogen dioxide to ferrocyanide:

$$K^6Fe^2Cy^{12} + H^2O^2 = H^2K^2FeCy^6 + K^4FeCy^6 + O^2,$$

on which reaction depends the blueing of a mixture of potassium ferricyanide and ferric chloride by hydrogen dioxide (ferric salts not being reduced thereby).—10. The *peroxides* of *potassium*, *sodium*, and *barium* are resolved by water into hydrates of the alkali-metal and hydrogen dioxide, which, however, is immediately decomposed by the alkali, and can therefore be detected in the solution only in small quantity. On the other hand, it may be supposed that the alkaline hydrates are converted by hydrogen dioxide into hydrated peroxides, which are again resolved, with evolution of oxygen, into alkali-hydrate, oxygen, and water; thus:

$$2KHO + 2H^2O^2 = 2KHO^2 + 2H^2O$$

and

$$2KHO^2 = 2KHO + O^2.$$

The rapid decomposition of hydrogen dioxide in all reactions in which alkalis are set free takes place in this manner, and is not due to catalytic action (Weltzien).

When a solution of *ferrous oxide* is mixed with *phenol* and then with hydrogen dioxide, the liquid becomes green, and if sufficiently concentrated yields a dark green precipitate of unknown composition; at the boiling heat, however, it deposits ferric hydrate.

A solution of *potassium dichromate* similarly treated gradually yields a dark brown precipitate; an ammoniacal cupric solution deposits cuprous oxide. In these reactions the reduction takes place only when the hydrogen dioxide is added *after* the phenol (J. Parnell, *Chem. Soc. J.* [2] vi. 356).

Hydrogen dioxide is decomposed by all *ferments*, especially by yeast, these bodies acting as deoxidisers; they lose this power however when heated with water to the boiling point (Schönbein, *J. pr. Chem.* cvi. 257; *Zeitschr. f. Chem.* [2] v. 533).

A solution of *guajacum* mixed with blood-corpuscles, or with infusion of malt, turns blue on addition of hydrogen dioxide, and affords a test for that compound exceeding in delicacy any yet proposed, and producing distinct indications in water containing not more than 1 pt. of it in ten million. By means of this reaction it may be shown that alcohol, ether, wood-spirit, acetone, and other organic liquids contain perceptible quantities of hydrogen dioxide, after being agitated for a few minutes with air in sunshine, and that this compound is instantly formed when zinc or other metals are oxidised in contact with water (Schönbein, *J. pr. Chem.* cv. 219; *Jahresb.* 1868, p. 145).

For the quantitative estimation of hydrogen dioxide, Houzeau (*Zeitschr. f. Chem.* [2] iv. 223) adds to the neutral solution, first dilute titrated sulphuric acid (containing 0·006125 grm. H^2SO^4 in 5 c.c.), then a slight excess of potassium iodide solution (containing 3 grm. of the salt in 100 grm. water); warms the liquid gently to facilitate the reaction; then boils it till all the iodine is expelled; and estimates the quantity of free acid still present with a standard soda-solution. Every cub. cent. of acid neutralised by the alkali from the potassium iodide corresponds to 0·431 milligrm. of hydrogen dioxide.

HYDROGEN PHOSPHIDES. According to Commaille (*J. Pharm.* [4] viii. 321), phosphoretted hydrogen gas is evolved by the action of phosphorus on potash-ley even at ordinary temperatures. Hence in determining carbon dioxide and oxygen in a gaseous mixture, by absorbing the former with potash-ley and then introducing a stick of phosphorus to absorb the oxygen, an error may arise in consequence of the phosphorus becoming wetted by the potash-solution, and then evolving phosphoretted hydrogen.

R. Mahn (*Zeitschr. f. Chem.* [2] v. 730) has examined the action of phosphoretted hydrogen gas, or phosphine PH^3, on the chlorides of phosphorus, antimony, and tin. With *phosphorus pentachloride* it reacts according to the equation, $PH^3 + 3PCl^5 = 4PCl^3 + 3HCl$, as previously shown by H. Rose. When passed into heated *phosphorus trichloride*, it slowly forms a red precipitate of phosphorus, as also shown by Rose. When passed into cooled *antimonic chloride*, it forms antimonious chloride, phosphoric chloride, and hydrochloric acid:

$$PH^3 + 4SbCl^5 = 4SbCl^3 + PCl^5 + 3HCl.$$

Passed into fused *antimonious chloride*, it forms a black precipitate consisting chiefly of antimony and phosphorus. With *stannic chloride* it forms a yellowish-red compound, $Sn^2Cl^6P^2$.

HYDROGEN SULPHIDE, H^2S, *Hydrosulphuric* or *Sulphydric acid*, is formed abundantly when hydrogen gas is passed through boiling sulphur (Merz a. Weith, *Zeitschr. f. Chem.* [2] v. 603); also when a succession of induction-sparks is passed through a mixture of hydrogen gas and sulphur vapour (Chevrier, *ibid.* 608).

According to J. Myers (*Zeitschr. anal. Chem.* 1869, 409), it is formed when aqueous vapour is passed over boiling sulphur, an acid liquid then distilling over which is a solution of sulphydric and pentathionic acids, the latter obviously resulting from the sulphydric acid and sulphurous anhydride simultaneously produced.

HYDROMECONIC ACID. See MECONIC ACID.

HYDROMELLITIC ACID. See MELLITIC ACID.

HYDROPARACOUMARIC ACID. See HYDROCOUMARIC ACID.

HYDROPHLORONE. See PHLORONE.

HYDROPHTHALIC ACID. See PHTHALIC ACID.

HYDROPIPERIC ACID. See PIPERIC ACID.

HYDROQUINONE. See QUINONE.

HYDROSALICYLAMIDE, $C^{21}H^{18}N^2O^3$, is converted by gentle heating with hydrochloric and hydrocyanic acids into yellow hydrocyanosalide, $C^{22}H^{16}N^2O^3$, and sal-ammoniac:

$$C^{21}H^{18}N^2O^3 + HCN + HCl = NH^4Cl + C^{22}H^{16}N^2O^3.$$

By washing the solidified product with alcohol, and crystallising it from a large quantity of the latter, hydrocyanosalide is obtained in interlaced orange-yellow needles. It is indifferent, very stable, insoluble in water, very slightly soluble in alcohol, and decomposed by potash, with evolution of ammonia and formation of resinous products. By boiling for several days with alcohol, it is gradually converted into brown needles of an isomorphous compound distinguished from the yellow modification by greater solubility and a different crystalline form.

Hydrocyanosalide is also formed, together with ammonium cyanide and its products of decomposition, when hydrosalicylamide is acted upon by hydrocyanic acid alone (Reinecke a. Beilstein, *Ann. Ch. Pharm.* cxxxvi. 169).

HYDROSOL. The name applied by Graham to the soluble hydrate of a colloïdal substance (v. 1088).

HYDROTEPHROITE. Hydrated manganous silicate from New Jersey, massive, light red, translucent on the edges, contains 28·46 p. c. SiO^2, 11·89 MgO, 53·44 MnO, 0·49 Mn^2O^3, and 5·85 H^2O (Igelström, *Jahresb.* 1867, p. 995).

HYDROTEREPHTHALIC ACID. See TEREPHTHALIC ACID.

HYDROXAMYLENE-AMMONIUM. $C^5H^{14}NO = \left.\begin{matrix} C^5H^{10}.OH \\ H^3 \end{matrix}\right\} N$ (Wurtz, *Ann. Ch. Pharm. Suppl.* vii. 89).—When the hydrochloride of amylic glycol is heated with excess of ammonia, the chloride of this base, $C^5H^{14}NO.Cl$ or $C^5H^{13}NO.HCl$, is formed, together with that of the corresponding valeryl-base, $C^5H^{12}NCl$ or $C^5H^{11}N.HCl$, derived from it by abstraction of water. On evaporating the resulting liquid to a syrup, dissolving it in absolute alcohol to remove sal-ammoniac, mixing the alcoholic solution with platinic chloride, and leaving the filtered liquid to evaporate, crystalline crusts of the platinochloride

$(C^5H^{12}N)^2.PtCl^4$ (isomeric with that of vinyl-trimethyl-ammonium) separate out, and by recrystallisation this salt may be obtained in rather large dark orange-coloured crystals soluble in water and alcohol. The mother-liquor of the preceding salt finally yields by spontaneous evaporation the platinochloride of hydroxamylene-ammonium, $(C^5H^{14}NOCl)^2PtCl^4$, isomeric with that of choline (p. 448), which by repeated crystallisation may be obtained in orange-red crystals, very soluble in water and in alcohol.

On mixing the syrupy liquid containing these two platinum salts with excess of very strong potash-solution, a thick oily liquid separates; and on subjecting the whole to distillation, there passes over with the aqueous vapour a base which separates from the alkaline liquid on saturation with potassium hydrate. The decanted oily liquid distils without decomposition, the greater part passing over between 160° and 170°, as a thickish strongly alkaline liquid soluble in water, and smelling of ammonia. The residue of the distillation solidifies on cooling to a crystalline mass. The two bodies thus obtained are doubtless the hydrates corresponding to the platinum salts above described.

HYDROXETHYLENE-TRIETHYLAMMONIUM. $C^8H^{20}NO = \left.\begin{matrix}C^2H^4.OH\\(C^2H^5)^3\end{matrix}\right\}N$ (Wurtz, *Ann. Ch. Pharm. Suppl.* vii. 88).—The chloride, $C^8H^{20}NOCl$, is obtained by heating hydroxychloride of ethylene with triethylamine:

$$(C^2H^5)^3N + C^2H^4(OH)Cl = \left.\begin{matrix}C^2H^4.OH\\(C^2H^5)^3\end{matrix}\right\}N.Cl.$$

It is easily soluble in water and in alcohol, crystallises in beautiful striated prisms, and forms with platinic chloride the salt $(C^8H^{20}NOCl)^2.PtCl^4$, which also crystallises well. The *aurochloride* $C^8H^{20}NOCl.AuCl^3$ is less soluble than the platinochloride, and separates from boiling water in splendid golden-yellow laminæ. The *hydrate* $C^8H^{21}NO^2 = C^8H^{20}NO.OH$ is a homologue of choline, $C^5H^{15}NO^2$.

HYDROXYBENZYLURIC ACID. $C^{16}H^{21}NO^5$ (Otto, *Ann. Ch. Pharm.* cxxxiv. 303; *Jahresb.* 1865, p. 354).—An acid produced by oxidation of hydrobenzyluric acid (p. 704) when an alkaline solution of the latter is exposed to the air. It is crystalline; has an offensive odour when moist; melts between 60° and 70°; is insoluble in cold water, but dissolves easily in alcohol, ether, and alkalis; and is precipitated white by lead, silver, and mercury salts; brown by ferric chloride. Its solution in strong sulphuric acid has a cherry-red colour. The calcium salt $C^{16}H^{19}CaNO^5 + 3H^2O$ is soluble in water, and crystallises with difficulty in needles. In a vacuum hydroxybenzyluric acid is gradually converted (perhaps with formation of an intermediate product, $C^{32}H^{40}N^2O^9$) into the less hydrated acid $C^{12}H^{19}NO^4$, which in contact with water reproduces the original acid. The calcium salt of the less hydrated acid, $C^{16}H^{17}CaNO^4, + 6H^2O$, is less soluble than that of normal hydroxybenzyluric acid. A barium salt, $C^{16}H^{17}BaNO^4$, has also been obtained.

HYDROXYBIBENZOIC ACID. $C^{14}H^{12}O^5$ (Otto, *loc. cit.*).—Produced, together with glycocine and benzyl alcohol, by boiling hydroxybenzyluric acid with alkalis:

$$2C^{16}H^{21}NO^5 + H^2O = 2C^2H^5NO^2 + 2C^7H^8O + C^{14}H^{12}O^5.$$

Both in the free state and in its salts it changes, as readily as hydrobenzoic acid, into benzoic acid. Its *calcium salt* dried at 100° has the composition $C^{14}H^{10}CaO^5$. The *ethylic ether*, $C^{18}H^{20}O^5 = C^{14}H^{10}(C^2H^5)^2O^5$, is a limpid liquid, boiling at 205°–207°, and having an offensive odour, recalling that of ethyl benzoate and of elder-flowers.

HYDROXYLAMINE. $NH^3O = N\left\{\begin{matrix}H^2\\OH\end{matrix}\right.$ (Lossen, *Zeitschr. f. Chem.* [2] i. 551; iii. 129; iv. 399).—A base intermediate between ammonia and ammonium hydrate, produced by the action of tin and hydrochloric acid on ethyl nitrate:

$$NO^3.C^2H^5 + 3H^2 = NH^3O + H^2O + C^2H^6O.$$

A mixture of 50 pts. ethyl nitrate, 120 pts. tin, and 50 pts. aqueous hydrochloric acid of sp. gr. 1·12 becomes hot after a short time, without perceptible evolution of hydrogen; and if the mixture be heated for a few minutes, the tin precipitated by hydrogen sulphide, and the filtrate evaporated, sal-ammoniac separates out first, and then the very soluble hydrochloride of hydroxylamine, which may be freed from admixed sal-ammoniac by solution in absolute alcohol and addition of alcoholic solution of platinic chloride: the concentrated alcoholic filtrate yields the pure hydroxylamine hydrochloride in long spicular crystals.

Hydroxylamine is also produced when nitric acid is treated in like manner with tin and hydrochloric acid; but it cannot be conveniently prepared in this way, for part of the nitric acid remains undecomposed, and in the subsequent concentration of the liquid, this portion, together with the hydrochloric acid present, forms nitrohydrochloric acid, which decomposes the hydroxylamine. This decomposition may indeed be prevented by precipitating the tin with sodium carbonate instead of hydrogen sulphide, the free acids being thereby neutralised, and the hydroxylamine salt remaining unaltered on evaporation; but the salt thus obtained is the nitrate of hydroxylamine, which is very difficult to crystallise and to separate from the ammonium nitrate likewise present.

Hydroxylamine may be formed by direct union of nitrogen dioxide and hydrogen, namely, by passing a stream of nitrogen dioxide through a series of flasks in which hydrogen is evolved by boiling tin with hydrochloric acid, or a series of glass cylinders containing tin and hydrochloric acid, together with a little solution of platinic chloride, whereby hydrogen is evolved at ordinary temperatures. The decanted solution freed from tin by hydrogen sulphide, and evaporated, yields a saline mass, consisting of hydroxylamine hydrochloride, sal-ammoniac, and a little ferrous chloride. This mass is washed with a little absolute alcohol to remove the ferrous chloride, then boiled with absolute alcohol, which dissolves the hydrochloride of hydroxylamine, with only a little sal-ammoniac; the latter is precipitated by alcoholic platinic chloride; and from the filtrate the hydroxylamine salt is precipitated by ether in small crystals which are purified by recrystallisation from absolute alcohol (Ludwig a. Hein, *Zeitschr. f. Chem.* [2] vi. 211). On the preparation of hydroxylamine, see also Maumené (*Compt. rend.* lxx. 147; *Zeitschr. f. Chem.* [2] vi. 187).

Hydroxylamine is a very volatile and easily decomposible base, and can be obtained only in solution. Its salts are decomposed by potash, with evolution of nitrogen and formation of ammonia, quickly in concentrated, gradually in dilute solutions. Solutions of hydroxylamine may however be obtained by decomposing the salts in other ways, an alcoholic solution, for example, by decomposing the nitrate dissolved in alcohol with alcoholic potash. Alkaline carbonates also separate hydroxylamine, with evolution of carbon dioxide. The solutions have an alkaline reaction, and precipitate many metallic salts; with the salts of lead, iron, nickel, and zinc, and with chrome-alum and common alum, they form precipitates insoluble in excess of hydroxylamine. With aqueous cupric sulphate, hydroxylamine forms a grass-green precipitate, which when boiled with water, is reduced, with evolution of gas, to cuprous oxide; an ammoniacal cupric solution is decolorised by it. Mercuric chloride is reduced to mercurous chloride, and if the hydroxylamine is in excess, to metallic mercury. Silver solutions yield a black precipitate, which is quickly reduced, with evolution of gas, to metallic silver. It also reduces acid potassium chromate. In many of these reactions the hydroxylamine appears to be completely decomposed, with formation of nitrogen or its monoxide.

The salts of hydroxylamine decompose when heated, with copious and sudden evolution of gas; most of them easily form supersaturated solutions; none of those yet examined contain water of crystallisation. The *hydrochloride*, $NH^3O.HCl$, crystallises from alcohol in long spicular crystals resembling urea; from water in large irregular six-sided tables, monoclinic according to v. Lang; it melts at 100°, and then decomposes, with violent evolution of gas, into nitrogen, hydrochloric acid, water, and sal-ammoniac. The *nitrate*, $NH^3O.HNO^3$, solidifies slowly by spontaneous evaporation to a radio-crystalline, very deliquescent mass, easily soluble in absolute alcohol, decomposing at 100°. The *sulphate*, $2NH^3O.H^2SO^4$, remains on evaporating a solution of the hydrochloride with an equivalent quantity of sulphuric acid. It is very soluble in water, is precipitated by alcohol in needles, and crystallises by slow evaporation in well-defined monoclinic crystals, mostly with numerous faces. The *phosphate*, $(NH^3O)^3H^3PO^4$, is sparingly soluble in cold water, and separates in small cubic crystals on mixing dilute solutions of sodium phosphate and an easily soluble salt of hydroxylamine. The *acetate*, $NH^3O.C^2H^4O^2$, crystallises from warm absolute alcohol in prisms very slightly soluble in water, melting at 87°–88°. The *oxalate*, $(NH^3O)^2C^2H^2O^4$, crystallises from water in shining triclinic prisms. The *picrate*, $NH^3O.C^6H^3(NO^2)^3O$, dissolves easily in water and alcohol, forming red solutions; less easily in ether and benzol, crystallising therefrom in lemon-yellow prisms melting at 100°.

Hydroxylamine unites directly with *hydrocyanic acid*, forming a compound isomeric with urea.

With *ethyl oxalate*, hydroxylamine forms two acids consisting of $C^2H^4N^2O^4$, or a multiple thereof:

$$2NH^3O + C^2O^4(C^2H^5)^2 = C^2H^4N^2O^4 + 2C^2H^6O.$$

One of these acids, called oxalo-hydroxamic acid, separates as hydroxylamine salt, $NH^3O.C^2H^4N^2O^4$, in thin laminæ, when an alcoholic solution of 1 mol. ethyl oxalate and somewhat more than 3 mol. hydroxylamine is boiled for a few minutes and then left to cool. The acid $C^2H^4N^2O^4$, separated from this salt by decomposition with hydrochloric acid, forms microscopic prisms sparingly soluble in cold water, and detonating at 105°. Its salts are sparingly soluble or insoluble in water, and detonate loudly at 130°–180°, or when moistened with strong sulphuric acid. The *hydroxylamine salt* decomposes slowly at 100°, detonates at 105°, and produces on paper or on the skin a reddish colour which is removed by the stronger acids. The *potassium salt* $C^2H^2K^2N^2O^4$ crystallises fron boiling water in nodular groups of crystals; the *sodium salt* $C^2H^2Na^2N^2O^4$ in small tables. The *calcium salt* $C^2H^2CaN^2O^4$, and the *zinc salt* $C^2H^2ZnN^2O^4$, are flocculent precipitates, gradually becoming granulo-crystalline, and quite insoluble in water. The *barium salt*, perhaps, $C^6H^8Ba^2N^6O^{12}$ (43 p. c. Ba), is nearly insoluble in water, forms microscopic lenticular crystals, and is decomposed by nitric acid, with formation of oxalic acid and carbonic acid (Lossen).

Diethyl Hydroxylamine. $C^4H^{11}NO = N\left\{\begin{matrix}(C^2H^5)^2 \\ OH\end{matrix}\right.$ or $N\left\{\begin{matrix}OC^2H^5 \\ C^2H^5 \\ H\end{matrix}\right.$ (Lossen, *loc. cit.*)—This ethylated base is formed, together with others, in the reduction of ethyl nitrate by tin and hydrochloric acid, the hydrochlorides of these bases being contained in the last mother-liquors after the sal-ammoniac and hydroxylamine hydrochloride have been removed as completely as possible. By converting these hydrochlorides, first into sulphates, then into oxalates, three kinds of oxalate crystals are obtained, the most abundant of which consist of the *acid oxalate of diethyl-hydroxylamine*, $C^4H^{11}NO.C^2H^2O^4$. This salt crystallises from water in stellate groups of shining prisms; from strong boiling alcohol in microscopic needles; when heated it decomposes, with evolution of ammoniacal vapours. The *neutral oxalate*, $(C^4H^{11}NO)^2.C^2H^2O^4$, obtained from the acid salt by precipitating half the acid with milk of lime, is insoluble in absolute alcohol, and crystallises from water in prisms apparently monoclinic. By decomposition with zinc sulphate, it yields the *sulphate* $(C^4H^{11}NO)^2.H^2SO^4$, which is precipitated by ether from solution in absolute alcohol, in very delicate microscopic crystalline laminæ. The *hydrochloride* is uncrystallisable, soluble in absolute alcohol, and precipitated therefrom by ether as a syrup. The *platinochloride*, $(C^4H^{11}NO.HCl)^2PtCl^4$, is soluble in water and in boiling absolute alcohol, and separates from the latter in large orange-red crystals. A *phosphate*, $(C^4H^{11}NO)^2H^3PO^4$, obtained by neutralisation, crystallises from water in prisms, from strong boiling alcohol in capillary needles.

The *base* $C^4H^{11}NO$, separated by mixing any of its salts with potash-ley, agitating with ether, and evaporating the ethereal solution, forms a strongly alkaline, mild-tasting syrup, easily soluble in water, and not easily volatilising with aqueous vapour. Its aqueous solution forms with ferric chloride, chrome-alum, cobalt nitrate, and lead acetate, precipitates insoluble in excess; with cupric sulphate, a bluish-white precipitate soluble in excess with violet-brown colour; it reduces silver nitrate on adding potash and heating; with mercuric chloride in the cold it forms a cloud, which dissolves very easily in excess, the solution yielding a copious precipitate on boiling.

The formation of diethyl-hydroxylamine is probably preceded by that of ethyl-hydroxylamine, as shown by the equations:

$$\underset{\text{Ethyl nitrate.}}{NO^2.OC^2H^5} + 3H^2 = 2H^2O + \underset{\text{Ethyl-hydroxyl-amine.}}{NH^2(OC^2H^5)}$$

and

$$\underset{\text{Ethyl-hydroxyl-amine.}}{2NH^2(OC^2H^5)} = \underset{\text{Hydroxyl-amine.}}{NH^2(OH)} + \underset{\text{Diethyl-hydroxyl-amine.}}{NH(C^2H^5)(OC^2H^5)}$$

Dibenzhydroxylamide. $N(C^7H^5O)^2OH$ (K. A. Heintz, *Zeitschr. f. Chem.* [2] v. 733).—Produced by heating dry hydroxylamine hydrochloride with twice its weight of benzoyl chloride to 110° for twelve hours in a vessel from which the air is excluded. On treating the brownish product with boiling water, as long as benzoic acid is thereby dissolved, there remains a heavy oil which solidifies on cooling, and dissolves for the most part in cold aqueous sodium carbonate, forming a solution from which hydrochloric acid throws down dibenhydroxylamide as a white flocculent very bulky precipitate, to be purified by repeated crystallisation from alcohol.

Dibenzhydroxylamide is insoluble in cold, nearly insoluble in boiling water, but easily soluble in alcohol, ether, carbon bisulphide, chloroform, and benzol. From its solutions, which have an acid reaction, it may be obtained in shining white needles, sometimes 2 or 3 centimetres long. It melts with decomposition at 156°–158°, giving off colourless vapours which strongly attack the mucous membranes. It dissolves very easily in alkalis, but the resulting compounds have not been obtained in definite form.

Tribenzhydroxylamide, $N(C^7H^5O)^2(OC^7H^5O)$, is obtained, though not quite pure, by crystallising from alcohol the portion of the product of the action of benzoyl chloride on hydroxylamine hydrochloride which is insoluble in cold aqueous sodium carbonate. It crystallises in small, white, extremely light needles, which melt at 143°–145°, and may be heated to 210° without decomposition.

Both di- and tri-benzhydroxylamide are decomposed by boiling with caustic or carbonated alkalis, the resulting solutions yielding with hydrochloric acid a precipitate of benzoic acid (K. H. Heintz, *loc. cit.*).

HYDROXYL-BIURET. See the next article.

HYDROXYL-UREA. $CH^4N^2O^2 = CH^3(HO)N^2O$ (Dressler a. Stein, *Zeitschr. f. Chem.* [2] v. 202).—Produced by transformation of hydroxylamine cyanate, which is formed by double decomposition of potassium cyanate with a salt of hydroxylamine, best with the nitrate. A quantity of hydroxylamine sulphate equivalent to that of the potassium cyanate to be used, is decomposed with barium nitrate; the filtered solution of hydroxylamine nitrate is evaporated to a syrup at a very gentle heat; this syrup is dissolved in 2 or 3 vol. of perfectly absolute alcohol; the liquid cooled to between —10° and —15°; and the potassium cyanate, dissolved in the smallest possible quantity of cold water, is added by successive portions, the additions being discontinued as soon as the temperature of the mixture has risen to between + 5° and + 10°, till it has again been cooled to —10°. By proceeding in this manner the solutions may be mixed without perceptible evolution of gas or formation of ammonia. A sample of the solution filtered from the separated saltpetre is then to be mixed with absolute ether, and if a watery layer then separates, more absolute alcohol must be added to the liquid till ether no longer separates a watery liquid, but only a crystalline precipitate (chiefly saltpetre). The alcoholic solution is then to be mixed with about 1½ time its volume of ether, the liquid again filtered as rapidly as possible, carefully evaporated over the water-bath to a small volume, and the hydroxyl-urea which separates on cooling, purified by recrystallisation from absolute alcohol.

Hydroxyl-urea is very soluble in water; crystallises on cooling from boiling alcoholic solutions in needles or rosette-shaped aggregations; dissolves less easily in cold absolute alcohol; and is precipitated from the latter by ether in microscopic rhombic laminæ, having their acute angles partially truncated. Its solutions are neutral to litmus-paper. It melts at 128°–130°, and is decomposed by prolonged fusion, giving off gas, yielding a sublimate of ammonium carbonate, and leaving a residue chiefly consisting of ordinary urea, which at higher temperatures yields its usual products of decomposition. Hydroxyl-urea is decomposed by boiling *potash-ley*, with evolution of ammonia; by fuming nitric acid, with abundant evolution of gas. A solution of hydroxyl-urea mixed with *silver nitrate* becomes turbid after a while, from separation of silver, and yields a silver speculum when heated; addition of ammonia causes immediate reduction. Heated solutions of hydroxyl-urea reduce *mercuric oxide* to metal, *chromic acid* to chromic oxide, *cupric oxide* on addition of potash to cuprous oxide. *Ferric chloride* colours the solution of hydroxyl-urea deep blue-violet; in aqueous solution the colour disappears quickly on standing, still more quickly on boiling; in alcoholic solution it is permanent, and with excess of ferric chloride nearly black, or in dilute solution dark green; all these colours are destroyed by addition of hydrochloric or nitric acid.

Salts of hydroxyl-urea have not yet been obtained, its solution in nitric or hydrochloric acid decomposing even by spontaneous evaporation over sulphuric acid.

Hydroxyl-biuret (?). $C^2H^5N^3O^3$ (Dressler a. Stein, *loc. cit.*).—When moderately concentrated aqueous solutions of hydroxylamine sulphate and potassium cyanate are mixed together, the potassium sulphate precipitated by absolute alcohol, the alcoholic solution carefully concentrated over the water-bath, then mixed with ether, and the decanted ethereal solution partially distilled and then left to evaporate over sulphuric acid, gases and ammonia are evolved, indicating decomposition, and ultimately a crystalline mass remains, which after recrystallisation from hot alcohol of 80 p. c. has the composition $C^2H^5N^3O^3$.

This body contains the elements of 2 mol. cyanic acid and 1 mol. hydroxylamine, and may be formed either by direct combination: $2CHNO + NH^3O = C^2H^5N^3O^3$, or by separation of 1 mol. hydroxylamine from 2 mol. hydroxyl-urea: $2CH^4N^2O^2 - NH^3O = C^2H^5N^3O^3$. Empirically it has the composition of hydroxyl-biuret,

$C^2H^4(HO)N^3O^2$. It dissolves in water and in aqueous alcohol, especially when warmed, but only slightly in absolute alcohol, even at the boiling heat. From the alcoholic solution, it is separated by ether in microscopic four-sided prisms, apparently obliquely rhombic. Its solutions are neutral to litmus-paper. It melts at 134°, and then decomposes suddenly, with phenomena similar to those which accompany the decomposition of hydroxyl-urea. Potash and fuming nitric acid act upon it as upon hydroxyl-urea. With *silver nitrate* it forms, on standing or warming, a white flocculent precipitate which dissolves in ammonia, the solution being gradually reduced in the cold, quickly on heating, with formation of a silver speculum. When a solution of hydroxyl-biuret is heated with *cupric oxide* not in excess, the two unite, forming light green microscopic capillary needles. *Alkaline cupric solutions* and *mercuric oxide* are reduced by it on heating. With ferric chloride it does not yield any characteristic reaction.

A solution of hydroxyl-biuret in dilute hydrochloric acid evaporated over sulphuric acid, leaves a mixture of hydroxyl-urea and ammonium chloride; the hydrochloric acid has therefore eliminated 1 mol. cyanic acid from 1 mol. hydroxyl-biuret:

$$C^2H^5N^3O^3 - CHNO = CH^4N^2O^2.$$

HYOSCYAMINE. On the preparation and properties of this alkaloïd see Rennard (*N. Repert. Pharm.* xvii. 91; *Jahresb.* 1867, p. 529).

According to Höhn a. Reichardt (*Ann. Ch. Pharm.* clvii. 98), hyoscyamine has the composition $C^{15}H^{23}NO^3$, and is resolved by boiling for several hours with saturated baryta-water into an acid (hyoscinic acid) isomeric with phloretic acid, and a base (hyoscine):

$$\underset{\text{Hyoscyamine.}}{C^{15}H^{23}NO^3} = \underset{\text{Hyoscinic acid.}}{C^9H^{10}O^3} + \underset{\text{Hyoscine.}}{C^6H^{13}N}$$

Hyoscinic acid crystallises in long glistening needles, melts at 104°–105°, and smells somewhat like benzoic acid. It is monobasic, its barium salt containing $(C^9H^9O^3)^2Ba + 2H^2O$.

Hyoscine was obtained as an oily liquid having a strong alkaline reaction, and crystallising over sulphuric acid. Its platinochloride contains $2(C^6H^{13}N.HCl).PtCl^4$.

HYPERSTHENE from Farsund yields by analysis 47·81 p. c. SiO^2, 10·47 Al^2O^3, 3·94 Fe^2O^3, 10·04 FeO, slight traces of manganous oxide, 25·31 MgO, and 2·12 CaO (= 99·69): hence the formula $6M''SiO^3.AlFeO^3$ (A. Remelé, *Zeitschr. f. Chem.* [2] iv. 412).

HYPOGÆIC ACID. $C^{16}H^{30}O^2 = \left.\begin{matrix}C^{16}H^{29}O\\ H\end{matrix}\right\}O = C^{15}H^{29}.COOH$.—The derivatives of this acid have been examined by H. Schröder (*Ann. Ch. Pharm.* cxliii. 22). To prepare the acid itself, and separate it from the arachidic and oleic acids by which it is accompanied in earthnut oil, the mobile straw-yellow oil extracted by carbon bisulphide from the seeds of *Arachis hypogæa* is saponified by boiling for several hours with dilute soda-ley; the white inodorous soap is decomposed by hydrochloric acid; the mixture of fatty acids thereby separated is dissolved in the exact quantity required of hot alcohol; and the solution is evaporated, this treatment being repeated till the alcoholic solution no longer deposits crystals on cooling. On finally evaporating it in a current of hydrogen, pure hypogæic acid remains in small white crystals melting at 33°.

Hypogaeic Dibromide, $C^{16}H^{30}Br^2O^2$, is formed by direct combination of hypogæic acid with 1 mol. bromine. To prepare it, bromine is dropped slowly, and with constant stirring, into hypogæic acid cooled with ice, till the colour of the bromine becomes permanent; and the crude product, which has become syrupy, is left for some time in a cool place to allow any excess of bromine to evaporate. It is then saponified in the cold with the exact quantity of potash-ley required; the gelatinous soap is dissolved in alcohol; and the solution, diluted with water and filtered, is decomposed by hydrochloric acid. The buttery compound thereby separated is washed with water till the acid reaction disappears, and then dried in a vacuum. Hypogæic dibromide is solid, uncrystallisable, yellow or brownish, melts at 29°, and is easily dissolved by alcohol and ether, but is insoluble in water. It is very unstable, and decomposes even during saponification if this process is performed with concentrated potash-ley or an excess of it, or if it is aided by heat. Its salts are uncrystallisable and difficult to prepare.

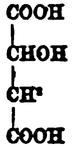
Bromohypogaeic acid, $C^{16}H^{29}BrO^2$, is produced by heating the dibromide in alcoholic solution with 2 mol. potassium hydrate:

$$C^{16}H^{30}Br^2O^2 + KHO = KBr + H^2O + C^{16}H^{29}BrO^2.$$

Amidodiglycollic acid also forms salts with the stronger acids. The *hydrochloride* $C^4H^7NO^4.HCl$ forms large, laminar, right rhombic prisms easily soluble in water, sparingly in alcohol. The *nitrate* $C^4H^7NO^4.NO^3H$ is a crystalline deliquescent mass. A solution of amidodiglycollic acid in 2 mol. sulphuric gradually deposits the neutral sulphate of amidodiglycollic acid, as a crystalline mass which is resolved by water or alcohol into the acid salt and free amidodiglycollic acid (Heintz, *Ann. Ch. Pharm.* cxxxvi. 213).

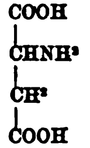
An acid isomeric with the preceding, which for distinction may be called diglycollamic (*Diglycollaminsäure*), is produced by treating diglycollimide (p. 649), with excess of warm baryta-water. The solution treated with carbonic acid, filtered, and evaporated, leaves an amorphous residue, from which hot alcohol extracts diglycollamic acid. The portion insoluble in alcohol is barium diglycollamate, $(C^4H^6NO^4)^2Ba + H^2O$, which, by covering the evaporated solution with a layer of alcohol, may be crystallised in small apparently oblique rhombic prisms This salt is neutral, moderately soluble in water, insoluble in alcohol and ether, decomposes above 145°, and is decomposed by prolonged boiling of its aqueous solution (more easily in presence of excess of baryta), giving off ammonia, and forming diglycollic acid, which is partly precipitated as barium salt. Diglycollamic acid separated from the barium salt by sulphuric acid forms unsymmetrical rhombic prisms of 84° 15. It is permanent in the air, moderately soluble in hot water, less in cold water and in alcohol, nearly insoluble in ether; melts above 125° to a mass which slowly solidifies and becomes opaque on cooling (Heintz, *Ann. Ch. Pharm.* cxxviii. 129; *Jahresb.* 1863, p. 364).

Amidodiglycollic and Diglycollamic acids are respectively isomeric with aspartic and malamic acids, which are amidated acids derived from malic acid. Aspartic and amidodiglycollic acids are bibasic; malamic and diglycollamic acids are monobasic. The constitutional formulæ of these acids, and their mode of derivation from malic and diglycollic acids, are indicated by the following formulæ:



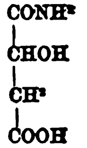
$$\begin{array}{l}COOH\\ |\\ CHOH\\ |\\ CH^2\\ |\\ COOH\end{array}$$

Malic.



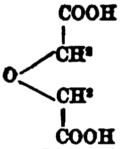
$$\begin{array}{l}COOH\\ |\\ CHNH^2\\ |\\ CH^2\\ |\\ COOH\end{array}$$

Aspartic.

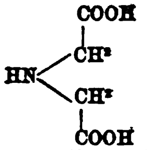


$$\begin{array}{l}CONH^2\\ |\\ CHOH\\ |\\ CH^2\\ |\\ COOH\end{array}$$

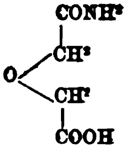
Malamic.



Diglycollic.

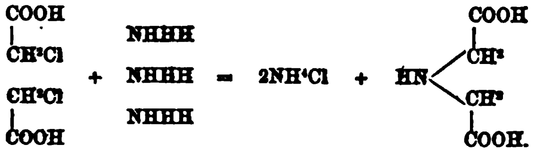


Amidodiglycollic.

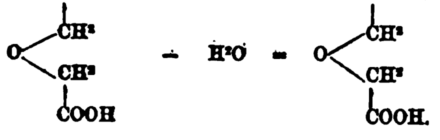


Diglycollamic.

The formation of amidodiglycollic acid by the action of ammonia (3 mol.) on chloracetic acid (2 mol.) is represented by the equation:



Diglycollamic acid, being formed by addition of 1 mol. H^2O to diglycollimide, $C^4H^5NO^3$—which is itself produced from acid ammonium diglycollate by abstraction of $2H^2O$—may evidently be regarded as formed from the same acid ammonium salt by abstraction of 1 mol. H^2O; thus:



ILMENIUM. For Hermann's investigations of the compounds of this element, which he supposes to exist, together with tantalum and niobium, in tantalites, &c., and for the criticisms of Marignac thereon, who regards Hermann's analytical methods as defective, and the separate existence of ilmenium as by no means proved, see *J. pr. Chem.* xcv. 65; xcix. 30, 279, 287, 290; ci. 459; cii. 399; cxi. 373; *Zeitschr. f. Chem.* [2] iii. 124, 125, 398; iv. 91; v. 311; *Jahresb.* 1865, p. 209; 1866, p. 207; 1867, p. 209; 1868, p. 216).

INDIGO. When indigo-blue is heated with tin and hydrochloric acid, a compound of indigo-white with stannous oxide is first formed, as a green powder which, on further heating, is converted into the yellow tin-compound of a further reduced indigo. This last compound, on account of its extreme oxidability, has not yet been isolated; in contact with the air it is immediately converted into a red body, soluble in alcohol, and resembling the condensation-products allied to indin. It is remarkable that this more completely reduced indigo cannot be reconverted into indigo-blue, although the first reduction-product, viz. indigo-white, immediately passes into indigo-blue in contact with the air. When the yellow tin-compound is triturated to a paste with water and zinc-dust, a green pulverulent mass is formed, the tin-compound being apparently converted into a zinc-compound, and this green substance when heated yields a considerable quantity of indol, $C^{8}H^{7}N$. The loss of colouring matter in the indigo-vat is perhaps due to the formation of the more highly reduced compound above mentioned (Baeyer, *Deut. Chem. Ges. Ber.* 1868, p. 17; *Zeitschr. f. Chem.* [2] iv. 200).

On the reduction of indigo-blue by stannous chloride and cuprous chloride, see C. D. Braun (*Zeitschr. anal. Chem.* vi. 74; *Jahresb.* 1867, p. 729); by cobaltous nitrate and ammonia, with simultaneous formation of roseo-cobaltic chloride: COBALT BASES, AMMONIACAL (p. 477).

Indigo-blue heated with 80 times its weight of saturated aqueous hydriodic acid is completely decomposed, yielding, as normal product, octane, $C^{8}H^{18}$, together with larger quantities of methane and heptane (Berthelot, *Jahresb.* 1867, p. 348).

For the valuation of commercial indigo-blue, Leuchs (*Zeitschr. f. Chem.* [2] v. 159) converts it into indigo-white by digestion with ferrous sulphate and milk of lime, mixes the clear solution, acidulated with sulphuric acid, with a solution of ammonio-ferric sulphate, and determines the quantity of ferrous salt thereby produced by means of a $\frac{1}{10}$ normal solution of potassium chromate. The conversion of indigo-white into indigo-blue by ferric salts takes place as shown by the equation:

$$C^{16}H^{12}N^{2}O^{2} + Fe^{2}O^{3} = 2FeO + H^{2}O + C^{16}H^{10}N^{2}O^{2}.$$

1·31 grm. of the sample of indigo is mixed, in a tall cylindrical well-closed vessel, with a quantity of lime and solution of ferrous sulphate occupying 300 cub. cent.; 100 c. c. of the clear solution are then added to $66\frac{2}{3}$ c. c. of a solution of ammoniacal iron-alum acidulated with sulphuric acid; the liquid is filtered, and 100 c. c. of it titrated with the $\frac{1}{10}$th chrome-solution. If the latter be added from a measuring tube divided into $\frac{2}{3}$ c. c., each division will correspond to 1 p. c. indigo-blue in the sample under examination.

Yellow Colouring Matter from Indigo.—Bengal indigo, either crude or purified, yields by sublimation a small quantity of a golden-yellow colouring matter, apparently free from nitrogen. It forms long needles which volatilise at about 130°; is nearly insoluble in water, very slightly soluble in alcohol, more easily in soda-ley, strong sulphuric acid, and nitric acid. The greenish-yellow alcoholic solution is decolorised by soda-ley (but not by ammonia); the solution in nitric acid is yellow (Bolley and Crinsoz, *Zeitschr. f. Chem.* [2] ii. 573).

INDIRETIN. $C^{16}H^{16}N^{2}O^{4}$.—A resinous substance produced, together with dioxindol, by the action of alcoholic potash upon isatane (p. 734); also by boiling isatin with tin and hydrochloric acid. By removing the tin with hydrogen sulphide, neutralising the filtrate with sodium carbonate, adding caustic soda till it turns yellow, agitating with ether, dissolving the evaporated residue of the ethereal extract in alcohol, and decolorising with animal charcoal, indiretin is obtained in the form of a resin, which gradually solidifies to a mass of prismatic needles, easily soluble in alcohol, ether, and potash, and precipitated from the latter by acids. The solutions smell like benzoic ether, and oxidise on exposure to the air. The silver-compound $C^{16}H^{14}Ag^{2}N^{2}O^{4}$ separates in yellow scales on mixing the alcoholic solution with ammoniacal silver nitrate (Knop, *J. pr. Chem.* xcvii. 65).

The name indiretin is also applied by Schunck to a resinous body, $C^{18}H^{17}NO^{3}$, produced, together with others, by the action of sulphuric acid on indican (iii. 268).

INDIUM. *Atomic Weight*, 75·63. *Symbol*, In. Bivalent, belonging to the magnesium group.

This metal, discovered in 1863 by Reich a. Richter (iii. 268), has since been further examined by the same chemists (*J. pr. Chem.* xcii. 480; *Chem. News*, x. 219; *Jahresb.* 1864, p. 240); also by C. Winkler (*J. pr. Chem.* xciv. 1; *Chem. News*, xi. 289; *Jahresb.* 1865, p. 231; *J. pr. Chem.* cii. 273; *Bull. Soc. Chim.* [3] ix. 207; *Jahresb.* 1867, p. 260); by Böttger (*J. pr. Chem.* xcviii. 26; cvii. 39; *Bull. Soc. Chim.* [2] vi. 452; *Jahresb.* 1866, p. 222; 1868, p. 240); and by R. E. Meyer (*Ann. Ch. Pharm.* cl. 137; *Bull. Soc. Chim.* [2] x. 18, 360; *Jahresb.* 1868, p. 241).

Indium is an extremely rare metal, occurring always in very small quantity, associated with zinc and other metals, from which it is separated with difficulty. It was originally discovered in the zinc-blende of Freiberg, and has since been found by Böttger in the flue-dust of the zinc-furnaces of the Julius works at Goslar in the Hartz (to the amount of about 0·1 p. c.); by Winkler in the black blende (christophite) of Breitenbrunn in Saxony (0·0062 p. c.); by Hoppe-Seyler (*Ann. Ch. Pharm.* cxl. 247) in small quantity, together with zinc, in the wolfram of Zinnwald, and in another specimen of wolfram of unknown origin; and by Köchler (*Jahresb.* 1865, p. 231) in the blende which occurs in the steatite (matrix of tin-stone) of Schönfeld, near Schlaggenwald.

Extraction.—Indium is more easily prepared from crude metallic zinc than from the original ore, as it passes over in the distillate obtained in the metallurgic distillation of the ore, but, not being very volatile, accumulates in the distilled metal more abundantly than in the zinc-dust, which is the first product of the distillation. Winkler prepares it by the following methods, depending upon its precipitation in the metallic state by zinc, as oxide or carbonate by barium carbonate, and as basic sulphate from solutions containing sulphuric acid by boiling with sodium acetate.

a. Granulated Freiberg zinc, which contains 0·0448 p. c. indium, together with small quantities of lead, arsenic, cadmium, and iron, is digested with dilute sulphuric or hydrochloric acid till it is nearly (but not completely) dissolved; the liquid is heated as long as it continues to give off gas; the residual metallic sponge, consisting chiefly of lead, but containing also the whole of the indium, together with arsenic, cadmium, and iron, is dissolved in nitric acid; the greater part of the lead is precipitated by sulphuric acid; and the filtered liquid, after being freed from all the metals precipitable by hydrogen sulphide from acid solution, is heated with potassium chlorate to convert the ferrous into ferric salt, and then precipitated with excess of ammonia. The washed precipitate of indium oxide containing iron and zinc is dissolved on the filter in warm dilute acetic acid, and the indium (together with a little iron and zinc) is precipitated from the filtrate as sulphide by sulphydric acid. To purify it, the precipitate is dissolved in dilute hydrochloric acid; the sulphydric acid is expelled by warming; the cooled liquid is agitated several times in a closed vessel with barium carbonate, whereby the indium oxide is completely precipitated in a few minutes; the washed precipitate is treated with hot dilute sulphuric acid; and the pure indium hydrate is precipitated from the filtrate by ammonia.—*β.* The metallic sponge remaining after treating the impure zinc with dilute sulphuric acid may also be triturated to a paste with an equal weight of strong sulphuric acid; the mixture left to itself till it becomes a dry friable mass; this mass heated to dull redness to expel the excess of sulphuric acid, then pulverised and thrown into cold water; the water gradually heated to the boiling point; the solution filtered from the lead sulphate, and precipitated by excess of ammonia; and the precipitate of ferruginous indium-oxide treated as above, or in the following manner: The solution of the crude oxide in hydrochloric acid is mixed with an equivalent quantity of sodium chloride and evaporated to dryness; the residue is dissolved in a large quantity of cold water; the solution saturated with hydrogen sulphide, whereby the greater part of the indium is separated *nearly* free from iron; and the acid filtrate is evaporated to dryness and treated in like manner; after the third precipitation the solution retains only traces of indium, together with ferrous oxide. (See also Böttger, *Jahresb.* 1868, p. 240.)

To detect indium in zinc-blende, and prepare it therefrom, Winkler precipitates the hydrochloric acid solution of the roasted ore with metallic zinc at the boiling heat; dissolves the precipitate in nitromuriatic acid; removes the arsenic, cadmium, &c., by hydrogen sulphide; and precipitates the indium as oxide by barium carbonate. Any iron that this precipitate may contain is removed by redissolution, heating with sodium sulphite, and digestion with barium carbonate in a closed vessel. The indium may also be precipitated from the original solutions either directly by barium carbonate, or from a solution containing sulphuric acid, by neutralisation with sodium carbonate till a precipitate begins to form, and addition of sodium acetate: it is then precipitated as a basic sulphate containing zinc.

Böttger prepares indium from the flue-dust of the Julius zinc-furnaces at Goslar (containing 0·1 p. c. of the metal) as follows. Six or eight pounds of the dust, also containing copper, iron, zinc, cadmium, arsenic, and thallium, together with charcoal and foreign substances derived from the chimneys, is boiled for half an hour with hydrochloric acid; the solution is strained through linen; and after it has been clarified by standing for some time, plates of zinc are immersed in it for about six hours, the liquid being continually stirred. The metallic precipitate thereby formed, containing copper, arsenic, cadmium, thallium, and indium (and perhaps also lead), is collected on a double filter, freed from the adhering ferruginous liquid by careful washing, then boiled for half an hour with a concentrated solution of oxalic acid; and the hot mixture is diluted with a large quantity of hot water, and filtered. The solution containing the oxalates of cadmium, thallium, and indium is supersaturated with ammonia; the gelatinous precipitate of indium hydrate is repeatedly boiled with ammonia to separate the cadmium and thallium still remaining, and washed till it no longer exhibits the spectrum of thallium. The indium oxide thus obtained is mostly pure; any iron that it may contain may be removed by Winkler's method.

According to Meyer, the separation of the last traces of lead and iron from indium oxide by Winkler's method is not complete. Meyer prefers the following method, based upon the reaction of indium salts with potassium cyanide. The solution of indium sulphate, previously freed from the greater part of the iron, is mixed with potassium cyanide till the bulky precipitate at first formed is redissolved, then diluted with water to ten times its volume, and heated to the boiling point, whereby the whole of the indium is separated as pure hydrate in the form of a heavy, amorphous, easily washed precipitate, whilst the iron remains dissolved as potassium ferrocyanide. A trace of lead which adheres to the precipitate can only be removed by dissolving it in sulphuric acid, expelling the excess of that acid by evaporation, and treating the residual sulphate with alcohol and a few drops of sulphuric acid, whereby the indium sulphate is dissolved, while the lead sulphate remains behind.

Metallic indium may be obtained in small quantities by reducing the oxide with hydrogen; its reduction by charcoal or carbonaceous fluxes requires a very high temperature and entails loss by volatilisation. For the preparation of larger quantities, sodium is the best reducing agent. The finely pulverised oxide is mixed in a porcelain crucible with an equal weight of sodium cut into thin slices; the mixture is covered with previously fused sodium chloride; and the porcelain crucible, placed within a covered earthen crucible, is heated in an air-furnace, moderately at first till the reaction is ended, and then to redness. On breaking up the mass when cold, a regulus of indium containing sodium is found, from which the greater part of the sodium may be separated by immersing it in cold water, pressing it together after the violent evolution of hydrogen is over, washing it with water, then with alcohol and ether, heating it in a porcelain crucible, and fusing it with potassium cyanide. The regulus thus obtained is brittle, of the colour of nickel arsenide, and still contains sodium. For further purification, a lump of the metal weighing 1 or 2 grams, and previously warmed, is dropped into a layer of fused sodium carbonate, about 2 millimetres deep, in a porcelain crucible. It then quickly liquefies, gives off vapours of sodium, and becomes covered with a film of indium oxide. If the flame be then removed, and the crucible left to cool, a pure and perfectly malleable regulus of indium is obtained. The reduction of indium chloride with sodium does not yield good results (Winkler). Böttger precipitates the indium by zinc, presses the spongy metal in hot water, then between filtering paper in a screw-press, and finally melts it with potassium cyanide.

Properties.—Indium is a silver-white metal, soft, ductile, compact, and destitute of crystalline structure. Its specific gravity is 7·421 at 16·8°, and is not altered by hammering or rolling. It melts at 176° without oxidising in contact with the air, but at a higher temperature it becomes covered with a grey film of suboxide, which subsequently exhibits iridescent colours and is finally converted into the yellow monoxide. At a bright red heat the metal burns with a violet flame and brown smoke, forming the same yellow oxide. It is much less volatile than cadmium or zinc, and cannot be distilled in a glass tube in a stream of hydrogen; moreover, the hydrogen which has passed over it does not burn with a blue flame. Its electrical relation to cadmium and zinc is represented by the series

$$-\mathrm{In} \qquad \mathrm{Cd} \qquad \mathrm{Zn}+$$

hence it is precipitated from its solutions by cadmium as well as by zinc, and is less easily oxidised than either of these metals in air containing carbonic acid. It is slowly dissolved by dilute sulphuric and hydrochloric acid, with evolution of hydrogen, quickly by strong hydrochloric acid; oxidised by nitric acid with evolution of nitrogen dioxide; and converted by strong sulphuric acid into a pulverulent anhydrous sulphate.

The *spectrum* of the indium flame exhibits, besides the violet line α and the blue line β (iii. 268), two fainter blue lines, if the burner be fed with hydrogen gas under pressure, instead of coal gas (Winkler). The wave-length of the α line is 0·000455 mm. (J. Müller, *Phil. Mag.* [4] xxx. 76).

Reactions.—Hydrogen sulphide precipitates indium completely from a solution of its acetate, and from neutral solutions of indium salts in general; from solutions slightly acidulated with a mineral acid partially, and from strongly acid solutions not at all; but an acid solution of an indium salt saturated with hydrogen sulphide becomes turbid on dilution and deposits indium sulphide. The lemon-yellow to fiery-yellow precipitate heated with ammonium persulphide turns white, sometimes dissolves partially, and separates on cooling as a white bulky precipitate. A solution of indium oxide in ammonium carbonate is also precipitated by hydrogen sulphide. (See further, p. 733.)

Ammonia, neutral sodium carbonate, and *acid sodium carbonate* produce white precipitates (in the last case with evolution of carbon dioxide) insoluble in excess of the precipitant; the presence of tartaric acid prevents the precipitation by ammonia. Caustic *potash* and *soda* produce a white precipitate of indium hydrate, soluble in excess, but the solution gradually becomes turbid at ordinary temperatures, and immediately on boiling or on addition of sal-ammoniac. *Ammonium carbonate* also produces a white precipitate soluble in excess, and reprecipitated on boiling. *Barium carbonate* precipitates indium completely. *Sodium phosphate* forms a white precipitate, soluble in caustic potash, but separating again immediately from the solution. *Potassium monochromate* forms a yellow precipitate. *Oxalic acid* forms a crystalline precipitate in concentrated neutral indium solutions, but the precipitation is never complete. *Potassium cyanide* forms a white precipitate of indium cyanide, soluble in excess, and forming a solution from which all the indium is precipitated on boiling in the form of hydrate. *Potassium ferrocyanide* forms a white precipitate; the *ferricyanide, potassium dichromate,* and *tincture of galls* do not precipitate indium salts.

Quantitative Estimation.—Indium is most conveniently estimated by precipitating it as hydrate with ammonia, dissolving the washed precipitate in hot dilute nitric acid, evaporating, igniting, and weighing the oxide thus obtained. The ignited oxide is not hygroscopic, and does not increase perceptibly in weight, even after prolonged exposure to moist air. For exact determinations it is not advisable to ignite the precipitated oxide, on account of the loss attending the burning of the filter. Precipitation by hydrogen sulphide does not give exact results, on account of the solubility of the indium sulphide.

For the exact quantitative separation of indium from iron, the following process must be adopted. The ignited oxides are weighed together, and converted into sulphates (which, if much iron is present, is best effected by fusion with acid potassium sulphate); the solution, at the boiling heat, is nearly neutralised with sodium carbonate; the free carbonic acid expelled by boiling; and the solution, when quite cold, is mixed with a quantity of potassium cyanide sufficient to produce a strong alkaline reaction. The solution, coloured red by formation of potassium ferricyanide, is diluted to ten times its volume, and heated to boiling (whereupon the ferricyanide is reduced by the excess of cyanide to ferrocyanide), and the precipitated indium oxide is further treated as above. In the liquid filtered therefrom, and evaporated, if a non-ferruginous potassium cyanide has been used, the iron may be estimated with concentrated sulphuric acid (Meyer).

Atomic Weight.—By converting the pure metal into anhydrous oxide, InO, the atomic weight was found, in three experiments, to vary between 75·67 and 75·76. By decomposing sodio-auric chloride with pure indium, and determining the quantity of gold thereby precipitated, the atomic weight of indium was found to be 75·46 and 75·60. Mean of all the experiments: In = 75·63 (Winkler).

Compounds of Indium.

Bromide. $InBr^2$.—Formed by heating metallic indium with rather more than an equivalent quantity of bromine in an atmosphere of dry carbon dioxide, and distilling off the excess of bromine. It is white, crystalline, and easily volatile (Meyer).

Chloride. $InCl^2$.—Indium immersed in chlorine gas becomes covered at ordinary temperatures with a white film; when heated in chlorine it melts to a brown mass, and at a higher temperature burns with a yellow-green light, forming indium chloride. This compound sublimes without fusion at an incipient white heat in soft white laminæ; in contact with the air it sublimes with partial decomposition, and formation of non-volatile oxychloride. The same decomposition takes place in the aqueous solution when evaporated at a temperature above 100° (Reich a. Richter; Winkler).

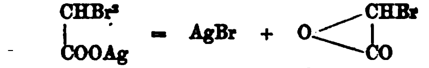
Indium chloride forms double salts with the chlorides of the alkali-metals. The *ammonium salt*, $4NH^4Cl.3InCl^2 + 2H^2O$, separates on evaporating a solution of equivalent quantities of indium oxide and sal-ammoniac, in small shining easily soluble crystals, permanent in the air. The *potassium salt*, $2KCl.InCl^2 + H^2O$, crystallises, together with potassium chloride, from a solution of equivalent quantities of its component salts, in thin plates which gradually change into six-sided prisms belonging to the quadratic system, and exhibiting the combination $\infty P . \infty P\infty . oP$, with P subordinate. Ratio of secondary to principal axis = 1 : 0·8196. Angle $P : oP = 130° 47'$; $P : \infty P = 139° 25'$. The *lithium salt* obtained in like manner crystallises in tufts of very deliquescent needles (Meyer).

Iodide. InI^2.—Prepared like the bromide. Yellow hygroscopic substance, easily melting to a dark brown-red liquid, distilling with difficulty, and solidifying to a crystalline mass (Meyer).

Oxides. Indium forms several oxides. The monoxide InO, obtained by igniting the nitrate or the precipitated hydrate, is of a pale yellow colour (dark yellow if it contains iron), becoming darker when heated. On igniting roasted indium sulphide with nitre and sodium carbonate, and removing the soluble salts by boiling with water, the monoxide remains in the form of a finely divided white powder. It is not volatile even at a white heat; dissolves in acids, with rise of temperature. By precipitating a cold solution of an indium salt with ammonia, the hydrate is obtained as a white gelatinous precipitate, which dries up in the air to horny lumps, and when ignited leaves the oxide in compact lumps of a light yellow to white colour. The hydrate precipitated at the boiling heat is compact and heavy, and yields an earthy oxide when ignited. The air-dried hydrate consists of $5InO.6H^2O$ or $5InH^2O^2.H^2O$, and is converted at 100° into the normal hydrate, $InO.H^2O$ or InH^2O^2.

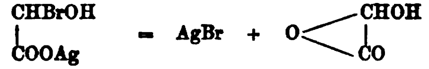
The monoxide heated in a stream of hydrogen becomes green or blue-green at 180°-190°, grey at 220°-230, deep black at 300°, and is reduced to the metallic state at a low red heat. The black oxide formed at 300° is *di-indic oxide*, In^2O. It is a light loose powder which, if exposed to the air while still warm, is converted quickly, but without incandescence, into the monoxide. It does not yield any metallic indium to mercury; is rapidly attacked by strong nitric acid, with evolution of nitrogen dioxide; and is dissolved by dilute acids with evolution of hydrogen. The green oxide appears to consist of $In^7O^6 = 5InO.In^2O$; the grey oxide of $In^6O^5 = 4InO.In^2O$; it has not, however, been proved that these two reduction-products are definite compounds. The green colour may perhaps be due to a trace of iron; in one instance of the incomplete reduction of very pure indium oxide, a light blue product was obtained (Winkler).

Oxygen-salts. The *nitrate*, $(NO^3)^2In + 3H^2O$, crystallises from an acid solution (with difficulty from a neutral) in long prisms or needles, which give off 2 mol. water at 100°, and when more strongly heated are converted into a basic salt previous to complete decomposition (Winkler). The *sulphate*, $SO^4In + 3H^2O$, remains on evaporating its aqueous solution at 100° as a gummy mass, and is converted, between 250° and 300°, into the spongy, tumefied anhydrous salt, which when heated to redness leaves first a sparingly soluble basic salt, and finally the anhydrous oxide (Winkler). The neutral *chromate* is an insoluble precipitate; the acid chromate remains as an uncrystallisable syrup when its solution is evaporated (Meyer). The *carbonate* is a white gelatinous precipitate, soluble in ammonium carbonate, precipitated therefrom by boiling, insoluble in the carbonates of the fixed alkalis; the white precipitate formed by the acid carbonates of potassium and sodium is likewise insoluble in excess of the reagent (Winkler). The *oxalate*, $C^2O^4In + 2H^2O$, is precipitated from neutral solutions by oxalic acid or alkaline oxalates, as a white crystalline powder sparingly soluble in cold, more soluble in boiling water, and separating therefrom in small transparent crystals. When ignited in a close vessel, it leaves the velvet-black suboxide In^2O; by ignition in hydrogen it is reduced to metallic indium (Winkler). The *acetate* is obtained, by dissolving the cold-precipitated hydrate in glacial acetic acid, and evaporating to the crystallising point, as a mass of white, interlaced, microscopic needles, but so easily decomposible that it cannot be obtained of constant composition. The *formate* is obtained, by evaporating a solution of the hydrate in which gives up nothing to water, but when treated with potash or baryta-water is converted into a bromoglycollate: hence this yellow powder appears to contain bromoglycollide, formed according to the equation:



Silver Dibromacetate. Bromoglycollide.

This reaction renders it probable that silver bromoglycollate when heated will also yield, not an acid, but an anhydride. In fact, when this salt is heated in a sealed tube with anhydrous ether, a yellow powder is formed quite insoluble in ether, and the ether does not acquire any acid reaction, whereas if glyoxylic acid had been formed, it would have dissolved in the ether and rendered it acid. The yellow powder is likewise insoluble in water, but when heated with baryta, it immediately yields the decomposition-products of glyoxylic acid, viz. oxalate and glycollate. These results indicate that the yellow powder contains glyoxylide, $C^2H^2O^3$, from which glyoxylic acid is afterwards formed by addition of the elements of water. The formation of the glyoxylide is represented by the equation,



Silver Bromoglycollate. Glyoxylide.

When dry silver bromoglycollate is heated in a sealed tube for several hours in the water-bath with absolute alcohol, a yellow powder is formed, together with a clear liquid which is perfectly neutral to dry litmus-paper, but instantly reddens the paper when moistened. On evaporating the alcohol, a neutral liquid is left perfectly soluble in water, and exhibiting when heated with lime-water the reactions of glyoxylic acid. This liquid is ethyl glyoxylate, formed according to the equations,

$$C^2H^2BrAgO^3 = AgBr + C^2H^2O^3$$

Silver Bromoglycollate. Gloxylide.

and

$$C^2H^2O^3 + C^2H^5OH = C^2H^3O^4.C^2H^5$$

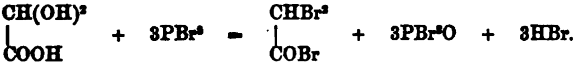
Glyoxylide. Alcohol. Ethyl glyoxylate.

This reaction seems to show that the body $C^2H^2O^3$ is an anhydride, and not glyoxylic acid; for in the latter case water would have been formed, and would have imparted an acid reaction to the liquid:

$$[C^2H^2O^3 + C^2H^5OH = C^2H(C^2H^5)O^3 + H^2O].$$

Glyoxylic acid (?).

A further argument in favour of the formula $C^2H^4O^4$ for glyoxylic acid is afforded by the behaviour of that acid with the pentachloride or pentabromide of phosphorus. Perfectly dry calcium glyoxylate distilled with phosphorus pentabromide yields hydrobromic acid, phosphorus oxybromide, and dibromacetyl bromide, which when dissolved in absolute alcohol, and treated with excess of water, yields ethyl dibromacetate:



$$\begin{matrix} CH(OH)^2 \\ | \\ COOH \end{matrix} + 3PBr^5 = \begin{matrix} CHBr^2 \\ | \\ COBr \end{matrix} + 3PBr^3O + 3HBr.$$

The compound $C^2H(NH^4)O^3$, from which Debus deduced the formula $C^2H^2O^3$ for glyoxylic acid, is regarded by Perkin a. Duppa as an amide which is converted into an ammonium salt when dissolved in water.

Dry sodium bromoglycollate heated to 120°–130° is gradually decomposed; and on treating the product with cold water, sodium bromide dissolves, and a white powder remains which dissolves in boiling water, forming a solution which exhibits the characters of glyoxylic acid. This white substance appears to be glyoxylide. It dissolves in ammonia, forming ammonium glyoxylate. Glycollide similarly treated yields glycollamide; and it might be expected that glyoxylide would also yield an amide; but the latter appears immediately to take up water, which converts it into an ammonium salt.

The following is a very characteristic reaction of glyoxylic acid: When a solution of calcium glyoxalate is mixed with aniline oxalate, and the liquid is filtered from calcium oxalate, a colourless solution is obtained, which when boiled, or even when left to itself for a few hours, deposits a bright orange-coloured precipitate (Perkin a. Duppa).

Indol is especially distinguished by the faculty with which it forms red compounds. On mixing its aqueous solution with fuming nitric acid somewhat considerably diluted, a red bulky precipitate separates, formed of small needles and probably consisting of indol nitrite, since it yields indol when boiled with water or alkalis. This red compound dissolves in alcohol, but is apparently decomposed thereby. The alcoholic solution of indol treated with nitrous acid yields large needles of another red body. The alcoholic solution mixed with hydrochloric acid colours fir-wood cherry-red, changing after a while to dirty brown-red.

Hydroxyl-derivatives of Indol (C. A. Knop, *J. pr. Chem.* xcvii. 65; *Jahresb.* 1865, p. 582. Baeyer a. Knop, *Ann. Ch. Pharm.* cxl. 1; *Jahresb.* 1866, p. 638).—Isatic acid, $C^8H^7NO^3$, has the composition of trioxindol, $C^8H^4(HO)^3N$, and this acid, or isatin, which is its anhydride, yields by reduction, dioxindol or hydrindic acid, $C^8H^7NO^2 = C^8H^5(HO)^2N$, and oxindol, C^8H^7NO or $C^8H^6(HO)N$, these three bodies being related to one another in the same manner as pyrogallic acid, oxyphenic acid, and phenol:

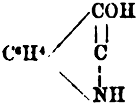
$$\underset{\text{Phenol.}}{C^6H^5(HO)} \qquad \underset{\substack{\text{Oxyphenic}\\\text{acid.}}}{C^6H^4(HO)^2} \qquad \underset{\substack{\text{Pyrogallic}\\\text{acid.}}}{C^6H^3(HO)^3}$$

$$\underset{\text{Oxindol.}}{C^8H^6N(HO)} \qquad \underset{\text{Dioxindol.}}{C^8H^5N(HO)^2} \qquad \underset{\text{Trioxindol.}}{C^8H^4N(HO)^3}$$

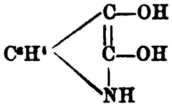
Isatin in acid solution is easily reduced to isatyde (iii. 411); and the latter is converted by sodium-amalgam into dioxindol, which again may be reconverted by oxidation into isatyde and isatin, so that isatyde is intermediate in composition between di- and tri-oxindol:

$$\underset{\text{Isatin.}}{C^8H^5NO^2} \qquad \underset{\text{Isatyde.}}{C^{16}H^{12}N^2O^4} \qquad \underset{\text{Dioxindol.}}{C^8H^7NO^2}$$

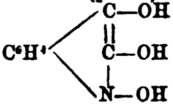
Baeyer a. Emmerling (*loc. cit.*) represent these compounds by the following constitutional formulæ, derived from their formula of indol (p. 733):



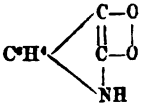
Oxindol.



Dioxindol.



Trioxindol (Isatic acid).



Isatin.

According to this view, isatin is a quinone, and in its potassium salt, $C^8H^4KNO^2$, the metal is in direct union with the nitrogen, as in the salts of maloxyl-urea and other derivatives of uric acid. Isatic acid is formed from it by resolution of the quinone-group, with simultaneous oxidation of the group NH; dioxindol is a hydroquinone, and oxindol a kind of phenol.

Kekulé (*Zeitschr. f. Chem.* [2] vi. 254) takes a somewhat different view of the constitution of indol and its derivatives. He considers it improbable that isatic acid can have the constitution of trioxindol, inasmuch as the successive reduction of this acid to indol requires the employment of three different reducing agents, which seems to imply that the three oxygen-atoms in this acid are united to the other elements in different ways. For Kekulé's views of the constitution of these compounds, see *Deut. Chem. Ges. Ber.* ii. 748; *Zeitschr. f. Chem.* [2] vi. 253.

DIOXINDOL or HYDRINDIC ACID, $C^8H^7NO^2$, is produced by the action of nascent hydrogen, generated by sodium-amalgam and water, on isatin, $C^8H^5NO^2$, or isatyde, $C^{16}H^{12}N^2O^4$; also by heating isatyde with alcoholic potash:

$$\underset{\text{Isatyde}}{C^{16}H^{12}N^2O^4} = \underset{\text{Isatin}}{C^8H^5NO^2} + \underset{\text{Dioxindol}}{C^8H^7NO^2};$$

and as a potassium salt, together with indiretin, by heating isatane with alcoholic potash to 130°:

$$\underset{\text{Isatane.}}{C^{32}H^{26}N^4O^6} + 2KHO = \underset{\substack{\text{Potassium-}\\\text{dioxindol.}}}{2C^8H^6KNO^2} + \underset{\text{Indiretin.}}{C^{16}H^{16}N^2O^4}$$

It is prepared by gradually adding sodium-amalgam to cold water in which isatin is suspended; the isatin then dissolves, and the action is complete when a sample of the liquid mixed with hydrochloric acid no longer yields a precipitate of isatin. The sodium salt, which separates after some days from the concentrated solution in warty crusts, is dissolved in water, neutralised with hydrochloric acid, and mixed with a saturated solution of barium chloride; and the barium salt which crystallises out is digested with a slight excess of sulphuric acid. The filtrate freed from sulphuric acid by addition of a little baryta-water, and evaporated as quickly as possible under the air-pump, yields dioxindol in groups of yellowish needle-shaped crystals. From a moderately concentrated solution it crystallises when left at rest in nearly transparent yellowish prisms, which, according to Rammelsberg, are monoclinic, exhibiting the combination $\infty P.(\infty P\infty).oP.+P.+nP\infty$, and having the clinodiagonal to the orthodiagonal as 1·012 : 1. Angle $\infty P : \infty P = 78° 40'$ and $101° 20'$; $(\infty P\infty) : \infty P = 129° 20'$; $oP : \infty P = 117°$, approximately. From hot alcohol it crystallises in dazzling white transparent crystals permanent in the air. It dissolves in 12 pts. cold and 10 pts. boiling absolute alcohol, also in a mixture of alcohol and ether. It decomposes when heated above 130°; melts at 180° to a violet liquid; and is converted at 195°, with evolution of a small quantity of aniline, into a rose-coloured amorphous mass. The light yellow aqueous solution becomes dark rose-red on exposure to the air, deeper red when heated, and then leaves a mixture of isatin and indin.

A solution of dioxindol in *hydrochloric acid* deposits dioxindol hydrochloride, $C^8H^7NO^2.HCl$, in large nodular crusts; from a solution in strong sulphuric acid, water throws down dioxindol sulphate, $C^8H^7NO^2.H^2SO^4 + H^2O$, in flocks which turn violet on exposure to the air, and appear crystalline when dry. Ammonia colours the solution violet, and on boiling throws down a violet colouring matter soluble in hydrochloric acid. The fixed alkalis and baryta produce a dark violet coloration, changing to red and finally to light yellow, just as with isatin or isatyde.

The metallic derivatives of dioxindol, or *hydrindates*, excepting the sodium salt, are sparingly soluble in water; they crystallise slowly and are precipitated in the crystalline state by a mixture of alcohol and ether; they are permanent in the air in the dry state, but oxidise quickly in solution. The following have been analysed:

Sodium salt,	$C^8H^6NO^2Na + 2H^2O$,	silvery scales.
Silver salt,	$C^8H^6NO^2Ag$,	yellowish-white precipitate.
Barium salt,	$(C^8H^6NO^2)^2Ba + 4H^2O$,	white cubic crystals.
Lead salt,	$(C^8H^6NO^2)^2Pb + 2H^2O$,	white crystalline precipitate.

When the moist silver compound is heated to 60°, drops of benzoic aldehyde separate, and the silver is reduced. Silver nitrate is also reduced by dioxindol, with formation of isatin. Dioxindol is attacked by *nitric acid*, more easily than isatin, with formation of decomposition-products.

A solution of dioxindol boiled for some time with *glycerin* deposits a violet-red amorphous powder, insoluble in boiling water, and isomeric with indin, $C^{16}H^{10}N^2O^2$ (iii. 264) (Knop).

When *chlorine* is passed into a cold-saturated alcoholic solution of dioxindol, chlorodioxindol, $C^8H^6ClNO^2$, first separates in yellowish needles, and afterwards dichlorodioxindol, $C^8H^5Cl^2NO^2$, in opaque scales. Aqueous dioxindol agitated with *bromine* deposits red laminæ of dibromodioxindol, $C^8H^5Br^2NO^2$, and the supernatant liquor yields on evaporation, light red crystalline groups of monobromodioxindol, $C^8H^6BrNO^2$ (Knop).

Nitrosodioxindol, $C^8H^6(NO)NO^2$, is produced by passing nitrous acid vapour into an alcoholic solution of dioxindol, but is converted by the prolonged action of the nitrous acid into ethyl benzoate. To prepare it, 10 pts. of absolute alcohol are saturated with nitrous acid, a concentrated alcoholic solution of 1 pt. dioxindol is added, and the whole is shaken up with 5 pts. of pulverised potassium carbonate till the mass becomes red and slightly warm. The powder when cold is washed with absolute alcohol and dissolved in water, and the product, precipitated with hydrochloric acid, is purified by repeated solution in potash, treatment with animal charcoal, and reprecipitation with hydrochloric acid.

Nitrosodioxindol forms a yellowish crystalline powder or interlaced needles, sparingly soluble in water, and crystallising therefrom in yellow brittle moss-like needles. It melts at 300°–310°, solidifies again in the crystalline form, and sublimes at 340° in white needles. When boiled with alcoholic ammonia it does not give the violet-red reaction characteristic of dioxindol. *Ammonium nitrosodioxindol*, $C^8H^5(NO)NO^2(NH^4) + 1\frac{1}{2}H^2O$, separates in white silky laminæ on evaporating the solution of nitrosodioxindol in very dilute ammonia. The *barium compound* $C^8H^4(NO)NO^2Ba$ is a white precipitate; the *silver compound* $C^8H^5(NO)NO^2Ag$ a yellowish-white precipitate.

Bromonitrosodioxindol, $C^8H^4Br^2(NO)NO^2 + 3H^2O$, is precipitated on mixing the aqueous solution of nitrosodioxindol with bromine-water, and crystallises from alcohol in tufts of needles. It dissolves without alteration in fuming nitric and sulphuric acids and in potash-ley, is not coloured violet by boiling with alcoholic ammonia, gives off its water at 140°, melts at 275°, and sublimes in white laminæ.

Azodioxindol, $C^8H^6N^2O$, is produced by boiling nitrosodioxindol with 6 pts. ferrous sulphate, excess of potash-ley, and a large quantity of water, and is precipitated from the filtered liquid by hydrochloric acid in white needles slightly soluble in water, easily in boiling alcohol, insoluble in hydrochloric acid. Bromine-water added to the aqueous solution throws down white flocks of a bromine-compound. It melts at 300°, but sublimes at 260° in colourless square plates. Its aqueous solution mixed with silver nitrate and ammonia yields a white crystalline precipitate of the compound $C^8H^4Ag^2N^2O^2$.

OXINDOL. C^8H^7NO.—Dioxindol cannot be further reduced in alkaline solution; but in acid solution it is reduced to oxindol by tin and hydrochloric acid, or better by sodium-amalgam. To prepare oxindol, isatin is first converted as above into dioxindol; the solution is diluted with water in the proportion of 100 pts. water to 1 pt. isatin, then acidulated with dilute sulphuric or hydrochloric acid, and heated in the water-bath; and sodium-amalgam is gradually added, keeping the acid always in excess. If after six hours the liquid remains light yellow, even when it has become alkaline, and an ethereal extract immediately yields needles on evaporation, it is neutralised with sodium carbonate and evaporated, till drops of oil make their appearance on the surface of the liquid. The oxindol which separates after 24 hours is purified by recrystallisation from hot water. It forms long colourless needles or feathery groups, melts at 120°, solidifies again at 110°, and at higher temperatures distils in small quantities without decomposition, as a colourless or reddish oil which immediately solidifies in the crystalline form. In hot water the crystals melt and dissolve abundantly, the liquid yielding crystals on cooling. On evaporating the concentrated solution, oily drops of fused oxindol separate on the surface; on exposure to the air, it is partly converted by oxidation into dioxindol. It dissolves in alcohol and ether, and crystallises therefrom in needles; forms a crystalline compound with potash, precipitates with salts of barium, copper, and calcium, and with basic lead acetate, and a specular deposit of silver when boiled with ammoniacal silver nitrate. *Silver oxindol*, C^8H^6AgNO, is formed on mixing a cold-saturated solution of oxindol with silver nitrate, and then with a little ammonia, as a precipitate which becomes granular on standing, and does not yield benzoic aldehyde when heated to 70°–80°. *Oxindol hydrochloride*, $C^8H^7NO.HCl$, is deliquescent, and forms groups of spicular crystals.

Bromoxindol, C^8H^6BrNO, separates on mixing the cold-saturated solution of oxindol with bromine-water, in white feathery crystals. It is insoluble in water, slightly soluble in alcohol, melts at 176°, and is precipitated by acids from the alkaline solution without alteration. *Tribromoxindol*, $C^8H^4Br^3NO + 2H^2O$, produced by adding bromine to the aqueous solution of oxindol, and removing the excess of bromine by heat, is insoluble in water, dissolves without alteration in potash, crystallises in feathery tufts, and decomposes without fusion at 270°.

Nitrosoxindol, $C^8H^6(NO)NO$, is formed on passing nitrous acid into a 1 per cent. aqueous solution of oxindol, till a sample of the liquid rubbed with a glass rod deposits crystals after a while. The liquid then solidifies immediately, or after 24 hours, to a pulp of very slender golden-yellow needles, which dissolve sparingly in water, more easily in alcohol, and with dark brown-red colour in potash. The compound decomposes when heated, yielding oily drops which smell like nitrobenzene. The *silver salt*, $C^8H^5(NO)NOAg$, is an orange-coloured gummy precipitate which detonates when heated.

Bromonitrosoxindol, $C^8H^5Br(NO)NO$, separates on mixing the cold solution of nitrosoxindol with bromine-water, in light yellow needles, slightly soluble in water, more easily in alcohol, and decomposing at 240° without fusion or sublimation. *Tribromonitrosoxindol*, $C^8H^3Br^3(NO)NO$, formed by treating the preceding compound with excess of bromine, is insoluble in water, easily soluble in hot alcohol, crystallises in needles of a dingy violet colour, melts at 162°, and sublimes at 190°.

Amidoxindol, $C^8H^6(NH^2)NO$, is formed by reducing nitrosoxindol with tin and strong hydrochloric acid. The acid solution, freed from tin by hydrogen sulphide and evaporated, yields colourless nodules of amidoxindol hydrochloride, $C^8H^6(NH^2)NO.HCl$. This salt is decomposed by water, with separation of a red resinous substance soluble in alcohol, gives off hydrochloric acid at 80°, and is completely decomposed at 170°, without previous fusion. Nitrosoxindol reduced with ferrous sulphate and potash yields a metallic-green colouring matter not yet examined.

Azoxindol. $C^8H^6N^2O$.—The sodium-derivative of this compound is formed by treating nitrosodioxindol with sodium-amalgam and a small quantity of water, as an amorphous mass, which, when decomposed by hydrochloric acid, yields azoxindol as an amorphous precipitate containing $2C^8H^6N^2O.H^2O$. It is slightly soluble in water, more easily in alcohol, from which it crystallises in cubes; it sublimes without fusion

1. When sulphocarbanilide is distilled, carbon bisulphide and hydrogen sulphide are given off, while an amorphous vitreous mass remains, consisting of triphenyl-guanidine mixed with aniline. The decomposition is represented by the following equations:

$$N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right. = N\left\{\begin{matrix}C^6H^5\\H^2\end{matrix}\right. + N\left\{\begin{matrix}CS\\C^6H^5\end{matrix}\right.$$

Sulphocarbanilide. Aniline. Sulphocarbanil.

$$N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right. + N\left\{\begin{matrix}CS\\C^6H^5\end{matrix}\right. = CS^2 + N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3\\H^2\end{matrix}\right.$$

Sulphocarbanilide. Sulphocarbanil. Triphenyl-guanidine.

$$N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right. + N\left\{\begin{matrix}C^6H^5\\H^2\end{matrix}\right. = H^2S + N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3\\H^2\end{matrix}\right.$$

Sulphocarbanilide. Aniline. Triphenyl-guanidine.

The decomposition begins below the boiling point of aniline, and after heating for several hours to 160°, considerable quantities of triphenyl-guanidine are obtained. Carbanilide, $N^2(CO)''(C^6H^5)^2H^2$, when thoroughly dry, splits up in the same manner, yielding triphenyl-guanidine, together with aniline, carbon dioxide, and water. The decomposition is represented by equations precisely similar to the above, the sulphur in each being replaced by oxygen.

2. Triphenyl-guanidine is also produced, as a hydrochloride, when sulphocarbanilide is fused with lead chloride:

$$3N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right. + PbCl^2 = 2\left[N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3.HCl\\H^2\end{matrix}\right.\right] + CS^2 + PbS.$$

On exhausting the product with a little alcohol, adding a large quantity of water, and evaporating the filtrate, the pure hydrochloride crystallises out.

3. Ammonium sulphocyanate heated with excess of aniline yields successively sulphocarbanilamide (phenylsulphocarbamide), sulphocarbanilide (diphenylsulphocarbamide), and triphenyl-guanidine; thus:

$$N\left\{\begin{matrix}CS\\NH^4\end{matrix}\right. + C^6H^5.NH^2 = NH^3 + N^2\left\{\begin{matrix}CS\\C^6H^5\\H^3\end{matrix}\right.$$

$$N^2\left\{\begin{matrix}CS\\C^6H^5\\H^3\end{matrix}\right. + C^6H^5.NH^2 = NH^3 + N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right.$$

$$N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right. + C^6H^5.NH^2 = H^2S + N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3\\H^2\end{matrix}\right.$$

4. Triphenyl-guanidine is likewise produced by heating sulphocarbanilide with metallic copper, cuprous sulphide being also formed, together with greasy secondary products consisting of hydrocarbons, probably resulting from the decomposition of methylene formed in the first instance:

$$3N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right. + 3Cu^2 = 3Cu^2S + CH^2 + 2N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3.\\H^2\end{matrix}\right.$$

5. Together with phenylsulphocyanate, when sulphocarbanilide is heated to 160°–170° with concentrated hydrochloric acid (Merz a. Weith):

$$N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right. + HCl = N\left\{\begin{matrix}C^6H^5\\H^2\end{matrix}\right..HCl + N\left\{\begin{matrix}CS\\C^6H^5\end{matrix}\right.$$

Sulphocarbanilide. Aniline hydrochloride. Phenyl sulphocyanate.

and

$$N^2\left\{\begin{matrix}CS\\(C^6H^5)^2\\H^2\end{matrix}\right. + N\left\{\begin{matrix}C^6H^5\\H^2\end{matrix}\right..HCl = H^2S + N^3\left\{\begin{matrix}C^{iv}\\(C^6H^5)^3.HCl\\H^2\end{matrix}\right.$$

Sulphocarbanilide. Aniline hydrochloride. Triphenyl-guanidine hydrochloride.

further addition of the chlorine solution, from formation of iodine chloride. If bromine is also present, the carbon bisulphide, immediately after decoloration, assumes an orange-yellow tint.

On the detection and estimation of iodine in presence of bromine and chlorine, see also p. 368.

The detection of iodine is often hindered by the presence of organic substances. According to Hlasiwetz (*Zeitschr. anal. Chem.* vi. 447), the aqueous solutions of resorcin, orcin, and phloroglucin take up iodine without coloration, or perceptible formation of hydriodic acid, in considerable but definite quantity, and withdraw it from its solution in carbon bisulphide. In these solutions the iodine can neither be detected by the ordinary reagents, nor volatilised by boiling. Nevertheless, the loose combination into which the iodine has entered is broken up when the solution is evaporated in a vacuum, the organic substance crystallising out in its original state, and the iodine subliming.

For the estimation of iodine in iodates and periodates, Rammelsberg (*Pogg. Ann.* cxxxv. 493) decomposes these salts with potassium iodide and dilute sulphuric acid, and titrates the separated iodine with sodium hyposulphite:

$$HIO^3 + 5HI = 3H^2O + 3I^2; \text{ and } HIO^4 + 7HI = 4H^2O + 4I^2.$$

On the estimation of iodine, see also Bobierre (*Zeitschr. f. Chem.* [2] v. 192); Struve (*ibid.* 383); Siewert (*ibid.* 307).

Hydriodic Acid. On the preparation of aqueous hydriodic acid by means of iodine and phosphorus, see Mich. Pettenkofer (*Ann. Ch. Pharm.* cxxxviii. 57; *Jahresb.* 1866, p. 138). According to Vigier (*Zeitschr. f. Chem.* [2] v. 412), the most suitable proportions for the preparation are represented by the equation

$$P^2 + 5I^2 + 5H^2O = P^2O^5 + 10HI.$$

Winkler (*J. pr. Chem.* cii. 33) passes hydrogen sulphide into an unsaturated solution of iodine in recently distilled carbon bisulphide, covered with a layer of water, and contained in a cylindrical vessel immersed in cold water. The passage of the gas must be continued till the liquid is decolorised, and the quantity of carbon bisulphide present must be sufficient to hold in solution all the separated sulphur. The hydriodic acid formed dissolves in the water, and may be obtained of any required degree of concentration by diminishing the quantity of the latter. After being freed from hydrogen sulphide by heating it for a short time in a retort, it is perfectly pure. A. Naumann (*Zeitschr. f. Chem.* [2] v. 436) modifies this process by leaving out the carbon bisulphide, and operating at first on a small scale, till the reaction becomes considerably accelerated by the solubility of the iodine in the hydriodic acid produced. The liquid is then cooled, and iodine and water are added from time to time as the action slackens. In this manner, even a very rapid stream of hydrogen sulphide is completely absorbed, and in a short time large quantities of hydriodic acid are obtained of sp. gr. 1·56. Of this acid only a small portion distils below 127°, the greater part remaining and exhibiting a sp. gr. of 1·67.

Reactions.—The decomposition of hydriodic acid by heat, and its action on various substances, have been examined by Hautefeuille (*Bull. Soc. Chim.* [2] vii. 198, 200, 203; *Jahresb.* 1867, p. 171). When the pure gaseous acid is gradually heated, it exhibits, at about 180°, a faint violet colour, indicating a commencement of decomposition, which increases slowly up to 440°, and rapidly between 440° and 700°, its amount being influenced by the extent of heated surface, and at a given temperature also by the pressure. Thus, when the gas was passed under ordinary pressure through a tube filled with fragments of glass, the decomposed portion amounted at 440° to 2·6, and at 700° to 34 p. c. On passing it through a glass tube filled with platinum-sponge, the results were:

At about	700°	440°	250°	195°	175°
Decomposed portion . .	22·2	19·5	18·7	17·5	10·5 p. c.

In a closed glass tube at the boiling point of sulphur:

Under a pressure of .	0·760	1·497	1·717	1·910	1·950 met.
Decomposed portion .	2·6	3·1	3·7	6·1	6·4 p. c.

Under constant pressure, therefore, the decomposition is considerably facilitated by the presence of platinum-sponge (below 180° iodine condenses on the surface of the platinum, and interferes with its action). When, on the other hand, a mixture of equal volumes of iodine-vapour and hydrogen is passed over heated platinum-sponge, the two elements partly combine, the uncombined portion being equal to that which is separated from pure hydrogen iodide by platinum-sponge at the same temperature.

Glass vessels are attacked by hydrogen iodide even below a red heat, with formation of water, an iodide of alkali-metal, hydrogen sulphide (from sulphur in the glass), and separation of iodine; the decomposition of the gas in glass vessels began at a lower temperature than in porcelain vessels. On the other hand, heated glass induces the formation of hydriodic acid from a mixture of iodine-vapour and hydrogen, to a small amount at 440° under ordinary pressure, more abundantly in closed tubes at the same temperature, the quantity of hydriodic acid formed increasing with the proportion of iodine present. Out of 100 c. c. hydrogen, there remained after heating with:

Iodine in milligr. . .	461	510	613	709	751	764	840	987	1351	4141
Uncombined H in c. c. .	62	54	45	46	37	35	36	26	14·8	5·7

In this case, therefore, as when platinum-sponge is used, a state of equilibrium is obtained, varying with the proportions of the reacting substances.

Sulphur decomposes gaseous hydriodic acid gas, or a cold-saturated aqueous solution, at ordinary temperatures, with formation of hydrogen sulphide and separation of iodine; dilute aqueous solutions only with aid of heat. These conditions are the reverse of those on which the preparation of aqueous hydriodic acid, by passing hydrogen sulphide into water containing iodine, depends. If the moderately concentrated aqueous acid be enclosed with sulphur in a glass tube, application of heat gives rise to the formation of hydrogen sulphide and separation of iodine, whereas on cooling, hydriodic acid is produced and sulphur separated, which after repeated alternations of temperature (between not very wide limits) crystallises in transparent octohedrons. When gaseous hydriodic acid is passed into *sulphur chloride*, hydrochloric acid is at first evolved, and iodine (or sulphur iodide) separated; afterwards hydrogen sulphide is formed in large quantity. *Selenium* acts on hydriodic acid in the same manner as sulphur, and the reaction may be made available for the preparation of hydrogen selenide, and of beautifully crystallised selenium. *Phosphorous chloride* and *arsenious chloride* exposed to a stream of the gas at ordinary temperatures are converted, with spontaneous rise of temperature and evolution of hydrochloric acid, into the corresponding iodine-compounds, which dissolve in the excess of chloride and finally crystallise out. Titanium chloride is decomposed at its boiling point; ammonium chloride at the temperature at which it volatilises; silicium chloride not below 440°.

These results show that a number of chlorides are decomposed by hydriodic acid at ordinary or at higher temperatures. On the other hand, metallic iodides (and bromides) are decomposed when strongly heated in excess of hydrochloric acid gas, silver iodide, for example, at about 700°. For the continuance of the decomposition, however, it is necessary that the hydriodic acid be removed as fast as it is formed: hence it appears that hydriodic acid can also decompose silver chloride at high temperatures. Lead iodide is decomposed by hydrochloric acid gas, even below its melting point; mercuric iodide and ammonium iodide are but slightly acted upon (Hautefeuille); compare Lieben (p. 437).

Nitrogen dioxide is slowly decomposed by concentrated aqueous hydriodic acid, with formation of ammonia and separation of iodine (Chapman a. Smith, *Chem. Soc. J.* [2] v. 166).

The reducing action of hydriodic acid on organic compounds has been elaborately investigated by Berthelot (*Bull. Soc. Chim.* [2] ix. 8, 91, 178, 265; *Jahresb.* 1867, p. 342), who has shown that all such compounds, except the paraffins, C^nH^{2n+2}, are decomposed by the concentrated aqueous acid, at sufficiently high temperatures, with formation of hydrocarbons. The products of the reaction vary with the proportion of hydriodic acid used; when it is pushed to its utmost limits, the only products (besides water, carbon dioxide, carbon monoxide, and ammonia) are paraffins, either containing the same number of carbon-atoms as the original substance, or formed from this substance by division. To ensure this complete reduction, however, the organic substance must be heated in a sealed tube for 10 to 24 hours to 270°–280°, with a saturated solution of hydriodic acid (sp. gr. = 2·0); alcohols and acids of the fatty series with 20 to 30 times, aromatic bodies with 80 to 100 times their weight of this concentrated acid; in general, the excess of acid required above the theoretical quantity is greater, as the proportion of hydrogen in the organic substance is less. With smaller quantities of hydriodic acid, intermediate products are obtained. The following are the principal results:

A. *Fatty Bodies.*—1. The *olefines* C^nH^{2n} are converted at ordinary temperatures, and more quickly at 100°, first into alcoholic iodides, then into paraffins; ethylene, for example, into ethyl iodide and ethane: $C^2H^4 + HI = C^2H^5I$; and $C^2H^5I + HI = I^2 + C^2H^6$.

2. The *hydrocarbons* C^nH^{2n-2}, homologous with acetylene, react in a similar manner: *e.g.*,

$$C^2H^2 + 2HI = C^2H^4I^2$$

and

$$C^2H^4I^2 + 2HI = 2I^2 + C^2H^6.$$

3. The *chlorine*, *bromine*, and *iodine derivatives* of the hydrocarbons likewise exhibit similar transformations; *e.g.*,

$$\underset{\text{Iodopropylene.}}{C^3H^5I} + 3HI = 2I^2 + \underset{\text{Propane.}}{C^3H^8}$$

$$\underset{\text{Perchlorethane.}}{C^2Cl^6} + 12HI = 6HCl + 6I^2 + \underset{\text{Ethane.}}{C^2H^6}$$

4. The *paraffins*, as already observed, remain unaltered under the influence of hydriodic acid, and constitute the ultimate products resulting from its action, unless they are decomposed by the heat.

5. *Alcohols* are converted, first into iodides and then into paraffins; *aldehydes* yield the same products, being first converted into alcohols. They however yield, together with the normal paraffin, small quantities of its lower homologues; thus acetic aldehyde yields ethane with a little methane; *acetone* yields chiefly propane, together with ethane and methane.

6. All the *acids*, *monobasic* or *polybasic*, of this group, are reduced under the above-named conditions—if they do not split up by themselves - to paraffins containing the same number of carbon-atoms; thus acetic acid yields ethane:

$$C^2H^4O^2 + 6HI = 2H^2O + 3I^2 + C^2H^6,$$

and butyric acid yields butane, C^4H^{10}. Formic acid yields only water and carbon monoxide, the latter not being attacked by hydriodic acid. Oxalic acid is resolved in like manner into carbon dioxide, carbon monoxide, and water. Succinic acid yields butane:

$$C^4H^6O^4 + 12HI = 4H^2O + 6I^2 + C^4H^{10}.$$

Tartronic acid, $C^3H^4O^5$, forms ethane and carbon dioxide, being first converted into malonic acid, $C^3H^4O^4$, which is then resolved into acetic acid and carbon dioxide. *Bibasic acids*, treated with a quantity of hydriodic acid not sufficient for complete reduction, are converted in great part into the corresponding monobasic acids, succinic acid, for example, into butyric:

$$C^4H^6O^4 + 6HI = 2H^2O + 3I^2 + C^4H^8O^2.$$

7. *Compound ethers* behave like their components, into which they are in the first instance resolved by assumption of water; ethyl formate, for example, yields carbon monoxide, water, and methane.

B. *Aromatic Compounds.*—*Benzene* heated for 24 hours to 280° with 80 parts of the aqueous acid is almost wholly converted into hexane; but at the same time a small quantity of propane is formed by splitting up of the benzene:

$$C^6H^6 + 8HI = 4I^2 + C^6H^{14}$$

and

$$C^6H^6 + 10HI = 5I^2 + 2C^3H^8.$$

With 15 to 20 pts. of the acid, benzene is resolved into carbon and propane:

$$2C^6H^6 + 6HI = 6C + H^2 + 3I^2 + 2C^3H^8;$$

with 30 to 40 pts. it appears to yield hexane, and in the first instance hexylene, which is afterwards resolved into difficultly volatile condensation-products. The chlorinated derivatives of benzene are first reduced to benzene, which then reacts with the excess of acid as above.

Phenol treated with insufficient quantities of acid is partly reduced to benzene, partly converted, with separation of carbon, into propane; with excess of acid it yields the same products as benzene.

Benzoic acid treated with 80 pts. hydriodic acid, yields heptane as normal product, and hexane in consequence of the resolution of the benzoic acid into carbon dioxide and benzene. With 20 pts. acid toluene is produced:

$$C^7H^6O^2 + 6HI = 2H^2O + 3I^2 + C^7H^8,$$

and in smaller quantities, benzene and carbon dioxide. *Benzoic aldehyde* with

20 pts. acid yields, as normal product, toluene, together with smaller quantities of benzene, xylene, and perhaps higher homologues.

Toluene heated with 80 pts. of this acid is completely converted into heptane, C^7H^{16}, with simultaneous abundant decomposition of hydriodic acid; heated with 20 pts. acid it yields charcoal and propane:

$$C^7H^8 + 2HI = 4C + H^2 + I^2 + C^3H^8.$$

Cumene, C^9H^{12}, is converted by 80 pts. acid into nonane, C^9H^{20}, with abundant decomposition of the hydriodic acid. With 23 pts. acid it yields charcoal and propane:

$$C^9H^{12} + 6HI = 3C + H^2 + 3I^2 + 2C^3H^8.$$

Cymene, $C^{10}H^{14}$, is converted by excess of the acid into decane, $C^{10}H^{22}$; *xylene*, C^8H^{10}, apparently into octane, C^8H^{18}.

According to Baeyer (*Zeitschr. f. Chem.* [2] iv. 445), hydriodic acid combined with *phosphine*, ($PH^3.HI$), does not act upon benzene even at 350°, but converts toluene into $C^7H^8.H^2$, xylene into $C^8H^{10}.H^4$, naphthalene at 170° into $C^{10}H^8.H^4$.

C. The more complex hydrocarbons allied to the aromatic group are partly resolved, by saturation with hydrogen, into several groups. *Diphenyl*, $C^{12}H^{10}$, treated with 80 pts. acid is almost wholly converted into hexane, C^6H^{14}; with 20 pts. of the acid, partly (to ⅔) into benzene, partly (to ⅓) into propane and charcoal:

$$C^{12}H^{10} + 2HI = I^2 + 2C^6H^6;\quad \text{and}\quad C^{12}H^{10} = 9C + H^2 + C^3H^8.$$

Cinnamene, C^8H^8, treated with 80 pts. of the acid yields, as chief product, an octane boiling at 115° to 120°, with small quantities of ethane and hexane:

$$C^8H^8 + 10HI = 5I^2 + C^8H^{18};\quad \text{and}\quad C^8H^8 + 12HI = 6I^2 + C^2H^6 + C^6H^{14}.$$

With 20 pts. of the acid, it is for the most part converted into cinnamene hydride, C^8H^{10} (? ethyl-phenyl), with benzene, ethane, and a difficultly volatile resinous hydrocarbon as secondary products:

$$C^8H^8 + 4HI = 2I^2 + C^6H^6 + C^2H^6.$$

Ethyl-phenyl, C^8H^{10}, and *bromethyl-phenyl*, C^8H^9Br, yield with 80 pts. of the acid, octane and small quantities of ethane and hexane.

Naphthalene, $C^{10}H^8$, may yield the hydrides $C^{10}H^{10}$, $C^{10}H^{12}$, $C^{10}H^{14}$, $C^{10}H^{22}$; also ethyl-phenyl and ethane; octane and ethane; benzene and ethane; hexane and ethane.

Anthracene, $C^{14}H^{10}$, treated with 80 pts. of the acid, yields as chief product, tetradecane, $C^{14}H^{30}$, together with heptane, hexane, ethane, and a paraffin boiling at 360°, perhaps $C^{28}H^{58}$. With 20 pts. acid it yields chiefly toluene, with small quantities of benzene, ethane, and a liquid hydrocarbon boiling at 260°, perhaps $C^{14}H^{12}$.

D. Bodies allied to the preceding hydrocarbons. *Alizarin* is converted by 20 pts. of the acid into a carbonaceous mass; by 100 pts. it is gradually but completely converted into paraffins, among which have been distinguished $C^{16}H^{34}$ (boiling at 270°–280°), one boiling above 360°, and in smaller quantity, hexane and ethane. *Phthalic acid*, $C^8H^6O^4$, with 10 pts. hydriodic acid yields heptane and octane:

$$C^8H^6O^4 + 14HI = CO^2 + 2H^2O + 7I^2 + C^7H^{16}$$

and

$$C^8H^6O^4 + 20HI = 4H^2O + 10I^2 + C^8H^{18}.$$

The isomeric compound *terephthalic acid* similarly treated yields only heptane.

E. Polymeric hydrocarbons treated with excess of hydriodic acid are partly converted into paraffins containing the same number of carbon-atoms, and are partly split up into simpler compounds, with addition of hydrogen; thus *polyethylene* (oil of wine), $C^{16}H^{32}$, boiling at about 280°, yields the paraffins $C^{16}H^{34}$, $C^{12}H^{26}$, C^6H^{14}, and C^2H^6. Similar results are obtained with the *polypropylenes* and *polyamylenes*. *Oil of turpentine*, $C^{10}H^{16}$, gives $C^{10}H^{22}$ and C^6H^{12}. With 20 pts. of the acid, decane, $C^{10}H^{18}$, is at first produced, and finally lower hydrocarbons of the same series, together with xylene.

F. Substances richer in carbon. *Bitumene* (p. 349) heated with 100 pts. of the acid is for the most part converted into hexane and an oily paraffin, $C^{16}H^{34}$ or $C^{24}H^{50}$. *Ulmin*, *wood*, and *wood-charcoal* are converted more or less completely into paraffins, the principal of which are $C^{12}H^{26}$, C^6H^{14}, and an oily body volatilising only at a red heat ($C^{24}H^{50}$?). *Coal* is attacked by 106 pts. of the acid, to the amount of about 60 p. c., and converted into similar hydrocarbons; the residue has the constitution of a resin. Graphite and charcoal ignited in a stream of chlorine are not attacked by hydriodic acid. But charcoal heated to whiteness in chlorine (after which treatment it may be regarded as pure carbon) dissolves slowly in strong nitric acid at 80°, forming a brown extractive substance which is acted upon by hydriodic acid like wood.

G. *Nitrogenous substances* heated with excess of hydriodic acid yield, as essential products, ammonia and saturated hydrocarbons. *Methylamine* yields ammonia and methane; *ethylamine*, ammonia and ethane; *aniline*, with 20 pts. of the acid, yields ammonia and benzene; *toluidine*, with 80 pts. acid, yields ammonia and heptane:

$$C^7H^9N + 12HI = NH^3 + H^2 + 6I^2 + C^7H^{16},$$

a large portion of the hydriodic acid being at the same time decomposed. *Methylaniline*, isomeric with toluidine, yields, under similar circumstances, methane and hexane; *ethylaniline*, ethane and hexane; *amylaniline*, quintane and hexane. *Amides* and *nitriles* are first converted, by assumption of water, into the corresponding ammonia-salts, after which the acid further decomposes. Respecting the reaction of hydriodic acid with *cyanogen* and *cyanides*, see pp. 521, 538; with *indigo*, p. 728.

Iodine Chlorides. The trichloride ICl^3 acts at ordinary temperatures on *carbon bisulphide*, forming a brown-red liquid containing sulphur chloride, carbon tetrachloride, and a crystallisable compound. The same products are formed when a solution of iodine in carbon bisulphide is saturated with chlorine gas. As the liquid cools, the compound separates in large well-defined prismatic crystals, having the colour of potassium dichromate, and so deliquescent that they can only be dried in a stream of dry chlorine gas and preserved in a sealed tube. When gently heated in a closed vessel they melt, giving off a small quantity of iodine chloride, and forming a liquid which solidifies in the crystalline form on cooling; they are decomposed by water and by hydrogen sulphide. These crystals have the composition $ICl^3.SCl^4$ (Weber, *Pogg. Ann.* cxxviii. 459; *Jahresb.* 1866, p. 138). Jaillard (*Jahresb.* 1860, p. 95), by passing chlorine over a mixture of iodine and sulphur, obtained a compound to which he assigned the formula $2ICl^3.SCl^2$; according to Weber, however, it is identical with that just described.

Iodine monochloride, ICl, added in aqueous solution to the acidulated hydrochlorides of various organic bases, forms crystalline compounds which separate as yellow precitates, and in some cases may be recrystallised without decomposition from dilute hydrochloric acid. The *tetrethylammonium compound* $(C^2H^5)^4NCl.ClI$ forms fern-like groups of needles, which are decomposed by water. The *triethylamine compound* crystallises in needles. The *caffeine compound* $C^8H^{10}N^4O^2.HCl.ClI$ is easily obtained pure, and forms crystals which appear to be oblique rhombic prisms. *Quinine hydrochloride* forms a yellow precipitate which assumes a dark colour when recrystallised from dilute hydrochloric acid (Tilden, *Chem. Soc. J.* [2] iv. 145).

Oxygen-acids of Iodine.

Iodic Acid. According to Stas (*Jahresb.* 1867, p. 162), the iodic acid prepared by decomposing barium iodate with dilute sulphuric acid always retains in solution a small quantity of barium sulphate, from which it cannot be freed. Perfectly pure iodic acid may be obtained by oxidising pure iodine with fuming nitric acid in a retort of glass not attacked by the acid,* evaporating to dryness, redissolving in water, again evaporating, and heating the white solid acid for some time to 200°, till it is converted into anhydride, and all the nitric acid is driven off with the water. The quantity of iodic acid thus obtained does not exceed ¼ pt. of the iodine used. If the oxidation is performed in a vessel of common glass, the iodic acid is contaminated with traces of soda and lime.

The following table of the specific gravity of aqueous iodic acid of different strengths is given by H. Kämmerer (*Pogg. Ann.* cxxxviii. 390; *Zeitschr. f. Chem.* [2] 277):

Percent. of I^2O^5	Sp. gr. at 14°	Percent. of I^2O^5	Sp. gr. at 14°
1	1·0053	40	1·5371
5	1·0263	45	1·6315
10	1·0525	50	1·7356
15	1·1223	55	1·8689
20	1·2093	60	1·9954
25	1·2773	65	2·1269
30	1·3484	100·5	4·7887 (at 9°)
35	1·4428		

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* Stas finds that an easily fusible glass not attacked by acids may be made by replacing half the potash in ordinary potash-lime glass with soda, such glass containing 77·0 p. c. SiO^2, 7·7 K^2O, 5·0 Na^2O, and 15·3 CaO (*Jahresb.* 1867, p. 920).

From a comparison of these densities with those of aqueous chloric acid, Kämmerer infers that the corresponding hydrates of the two acids occupy equal atomic volumes:

Formula of the Hydrate	Percent. of Anhydride	Molecular Weight	Sp. gr.	Atomic Volume
$HClO^3.7H^2O$	35·73	210·5	1·262	166·7
$HIO^3.7H^2O$	55·3	304	1·8256	165·4
$HClO^3.15H^2O$	21·29	354·5	1·161	305·2
$HIO^3.15H^2O$	37·44	446	1·489	299·5
$HClO^3.20H^2O$	16·98	444·5	1·128	394·2
$HIO^3.20H^2O$	31·16	536	1·389	391·6

Periodic Acid (Lautsch, *J. pr. Chem.* c. 65. Fernland, *ibid.* c. 99. Rammelsberg, *ibid.* ciii. 278; civ. 434; *Pogg. Ann.* cxxxiv. 134, 368, 499. *Jahresb.* 1867, pp. 162, 166; 1868, p. 162. Kämmerer, *loc. cit.*).—Kämmerer prepares this acid by decomposing the silver salt with chlorine, or better with bromine. The solution evaporated in a vacuum leaves the pure acid H^5IO^6 or $I^2O^7.5H^2O$. Lautsch confirms the observation of Langlois (iii. 308) that periodic acid $I^2O^7.5H^2O$ or H^5IO^6 melts at 130°, and is converted into iodic anhydride, I^2O^5, by loss of water and oxygen, between 200° and 210°. He finds, however, that the pure acid effloresces rather quickly in the air at ordinary temperatures. According to Rammelsberg, on the other hand, the crystals of periodic acid remain quite unaltered when left over sulphuric acid or when heated to 100°; they melt between 130° and 136°, and are completely resolved, even at that temperature, into iodic anhydride, oxygen, and water. Neither periodic anhydride, I^2O^7, nor the normal monohydrate HIO^4 has yet been obtained.

The basicity of periodic acid is still a matter of discussion. Rammelsberg regards it as monobasic, and classifies the metallic periodates as follows:

1. *Normal Periodates.*

$$\overbrace{MIO^4 \qquad M''I^2O^8}$$

KIO^4	$NaIO^4$	$SrI^2O^8 + 6H^2O$
$(NH^4)IO^4$	$LiIO^4$	$MgI^2O^8 + 10H^2O$
	$AgIO^4$	CdI^2O^8

2. *Three-fifths Periodates.*

$$M''^5I^6O^{26} = \begin{cases} M''I^2O^8 \\ 2M''^2I^2O^9 \end{cases}$$

$Ba^5I^6O^{26} + 18H^2O$
$Sr^5I^6O^{26} + 14H^2O$

3. *Four-sevenths Periodates.*

$$M''^7I^8O^{35} = \begin{cases} M''I^2O^8 \\ 3M''^2I^2O^9 \end{cases}$$

$Ni^7I^8O^{35} + 49(63)H^2O$

4. *Hemi-periodates*

$M^4I^2O^9$	$M''^2I^2O^9$
$K^4I^2O^9$	$Ba^2I^2O^9$
$K^4I^2O^9 + 9H^2O$	$Ba^2I^2O^9 + 6H^2O$
$(NH^4)^4I^2O^9 + 3H^2O$	$Ba^2I^2O^9 + 7H^2O$
$Na^4I^2O^9 + 3H^2O$	$Sr^2I^2O^9 + H^2O$
$Li^4I^2O^9 + 3H^2O$	$Sr^2I^2O^9 + 4H^2O$
$Ag^4I^2O^9 + 3H^2O$	$Ca^2I^2O^9 + 9H^2O$
$Ag^4I^2O^9 + H^2O$	$Mg^2I^2O^9 + 15H^2O$
	$Zn^2I^2O^9 + 6H^2O$
	$Cu^2I^2O^9 + 6H^2O$
	$Cd^2I^2O^9 + 9H^2O$

5. *Two-fifths Periodates.*

$$M''^5I^4O^{19} = \begin{cases} 3M''^2I^2O^9 \\ M''^4I^2O^{11} \end{cases}$$

$Ba^5I^4O^{19} + 12H^2O$
$Zn^5I^4O^{19} + 14H^2O$

6. *Three-eighths Periodates.*

$$M''^8I^6O^{29} + \begin{cases} 2M''^2I^2O^9 \\ M''^4I^2O^{11} \end{cases}$$

$Ba^8I^6O^{29} + 20H^2O$
$Ca^8I^6O^{29} + xH^2O$

7. *Trito-periodates.*

$M''^3I^2O^{10}$

$Pb^3I^2O^{10} + 2H^2O$
$Cd^3I^2O^{10} + 5H^2O$ (?)

8. *Tetarto-periodates.*

$M''^4I^2O^{11}$

$Mg^4I^2O^{11} + 6H^2O$
,, $+ 9H^2O$
$Zn^4I^2O^{11} + H^2O$
$Cd^4I^2O^{11} + 3H^2O$
$Cu^4I^2O^{11} + 7H^2O$
$(2Hg)^4I^2O^{11}$

9. *One-fifth Periodates.*

M^5IO^6	$M''^5I^2O^{12}$
H^5IO^6	$Ba^5I^2O^{12}$
Na^5IO^6	$Sr^4I^2O^{12}$
Li^5IO^6	$Ca^5I^2O^{12}$
Ag^5IO^6	$Hg^5I^2O^{12}$
	$Cu^5I^2O^{12} + 5H^2O$

10. *One-sixth Periodates.*

$Fe^4I^2O^{13} + 21H^2O$

the gutta-percha is exposed to light and to the alternate action of air and water. Gutta-percha kept under pure water or sea-water retains its original properties for a long time; but if exposed in sunshine to the alternate action of air and water, it gradually increases in weight, becomes brittle, resinous, more soluble in alcohol and in dilute alkalis. Pure milk-white gutta-percha, perfectly soluble in benzol, ether, and carbon bisulphide, has the composition of a hydrocarbon, $C^{20}H^{32}$. Heated to 100° it softens and gradually takes 4·4 p. c. oxygen, becoming brown, resinous, and brittle; the oxidised portion is insoluble in benzol. Commercial gutta-percha, such as is used for the manufacture of cables, becomes liquid at 100°, and contains, together with the pure hydrocarbon and mechanically enclosed water, a considerable quantity of the resinous oxidation-product, as shown by the following analysis:

Hydrocarbon	Resin	Woody fibre	Water	Ash	
79·70	15·10	2·18	2·5	0·52	= 100.

After drying at 100° it exhibited the composition A; the oxidised portion soluble in alcohol had the composition B; the portion soluble in benzol, and precipitable therefrom by alcohol, had the composition C:

	Carbon	Hydrogen	Oxygen	
A . . .	84·66	11·15	4·19	= 100.
B . . .	76·15	11·16	12·69	= 100.
C . . .	87·22	12·04	0·74	= 100.

Commercial gutta-percha, if excluded from light, may also be kept for months or even years under water or in air; but when it is exposed to light in the open air, the portions on which the light falls quickly assume the composition above given.

H

HÆMATEÏN. See HÆMATOXYLIN (*infra*).

HÆMATIN. See BLOOD (p. 355).

HÆMATOÏDIN. This substance, originally found in blood and afterwards in bile (iii. 3), is most easily obtained, according to Hulm (*Bull. Soc. Chim.* [2] viii. 60), from the *Corpus luteum* of the cow. According to Piccolo a. Lieben, however, the dichroic crystals obtained from the latter source are not identical with hæmatoïdin. These chemists also consider it most probable that hæmatoïdin is identical with bilirubin, and propose to designate the new substance from the *Corpus luteum* as luteohaematoïdin or haemolutein (p. 497). Jaffé (*Jahresb.* 1862, p. 537) finds that hæmatoïdin (from the brain of an apoplectic patient) exactly resembles bilirubin in its reaction with nitric acid, becoming first green, then blue, violet, &c.

HÆMATOXYLIN. $C^{16}H^{14}O^{6}$.—A solution of this substance, or paper saturated with it, is recommended by Wildenstein (*Zeitschr. anal. Chem.* ii. 9) as a test-paper, especially for the detection of ammonia, the fixed alkalis, alkaline earths, and certain metals (iii. 5). Swedish filtering paper thus prepared has a yellowish colour when dry, and is coloured red, violet, or violet-blue by the smallest trace of an alkali.

As hæmatoxylin reduces silver salts, it may be used, like pyrogallic acid, for developing photographic pictures. A solution for the purpose may be prepared with 0·5 pt. hæmatoxylin, 80 pts. distilled water, and 22 pts. acetic acid: a little glycerin may also be advantageously added (Tabensky, *Zeitschr. f. Chem.* [2] v. 386).

Haematein may be quickly prepared by passing air containing ammonia, by means of an aspirator, into a bottle containing hæmatoxylin suspended in water, the delivery-tube terminating just above the surface of the liquid: by this arrangement, an excess of ammonia is avoided, which would produce a brown amorphous substance. When a considerable quantity of hæmatoxylin is used, it may be simply drenched with ammoniacal water. The process yields a solution having a fine violet colour, and forming with acid ammonium sulphite a precipitate soluble at the boiling heat (Tabensky).

According to Schützenberger a. Paraf (*Jahresb.* 1862, p. 495), the violet solution of hæmatoxylin in ammonia is decolorised by heating to 100° for 48 hours in an exhausted tube, a colourless pasty mass being formed, which the authors designate as haematinamide; on exposure to the air it quickly takes up oxygen, and turns violet. It is slightly soluble in water, easily in alcohol, ether, and hydrochloric acid, and is precipitated from the latter by ammonia in white flocks.

HÆMIN. } See Blood (pp. 352, 356).
HÆMOGLOBIN. }

HÆMOLUTEIN. See Corpus Luteum (p. 497).

HAGEMANNITE. A fluoride occurring at Arksutfiord in Greenland, together with cryolite and pachnolite. It is opaque, has an ochre-yellow or wax-yellow colour, and uneven fracture; hardness = 3 to 3·5; sp. gr. 2·59 to 2·60. Contains:

Al	Fe	Ca	Mg	Na	F	Si	H^2O	Insol.
12·06	5·96	11·18	2·30	8·45	40·30	7·79	10·44	1·08

(Shepard a. Hagemann, *Sill. Am. J.* [2] xli. 119).

HEAT. Thermometry.—A convenient form of *air-thermometer*, for the approximate measure of temperatures above 300°, has been contrived by Berthelot (*Ann. Ch. Phys.* [4] xiii. 144, and xv. 413). It consists of a cylindrical bulb of glass or silver, with thin sides, of about 4 cubic centim. capacity, communicating at the upper end with a capillary tube of uniform bore, about 1·2 metre long and 0·2 mm. in diameter. At a distance from the bulb of about 200 mm. this capillary stem is bent so as to become horizontal, and at about 250 mm. further on it is bent downwards at a right angle, and, after proceeding vertically downwards for a length of about 730 mm., it is again bent up, and terminates in a wide open bulb. A double graduation is attached to the vertical part of the stem: on one side a scale of millimetres, and on the other a scale of thermometric degrees. These two scales are both divided upon a flat strip of wood, which is supported so as to be capable of being moved a short distance up or down the stem, and then clamped in any required position. The bulb and stem having been made thoroughly dry, a small quantity of pure dry mercury is poured into the bulb at the lower end of the stem, and by means of an air-pump the pressure in the bulb is reduced to 20 or 25 centim. of mercury; in this way part of the air is removed from the thermometer, and on restoring the atmospheric pressure, mercury is driven up towards the top of the vertical part of the stem. If the thermometer is to be used for indicating temperatures near 500°, the quantity of air removed ought to be such that a difference of temperature of 1°, at ordinary atmospheric temperatures, makes a difference of about 1 mm. in the height of the mercury in the stem. The thermometer is graduated empirically by marking on the scale the points at which the mercury stands in the stem when the bulb is surrounded by *ice*, and by the vapours of *boiling water*, *boiling mercury*, and *boiling sulphur* respectively. These points being marked 0°, 100°, 350°, and 440°, the intermediate temperatures, as well as temperatures below 0° and above 440°, are supplied by inter- and extrapolation. It is evident that the four fixed points must be determined when the barometric pressure is sensibly constant. Berthelot does not admit greater variations than 1 mm. of mercury. When the instrument is used to indicate unknown temperatures, the barometric pressure will in general be different from that under which it was graduated; but the requisite adjustment can be made by immersing the bulb in pounded ice, and pushing the graduated scale up or down the stem until the zero-mark agrees with the extremity of the mercury-column.

The action of the apparatus is easily understood by reference to the laws of the expansion of air. With the dimensions of bulb and stem that have been indicated, the changes of volume of the air in the thermometer consequent on the mercury standing at different heights may be neglected without sensible error; hence, if H_0 be the pressure (measured in millimetres of mercury) which the air supports at 0°, and $H_0 + h$ the pressure supported by it at $t°$, we have the equation (comp. iii. 49)

$$H_0 + h = H_0(1 + at),$$

whence

$$1 + \frac{h}{H_0} = 1 + at,$$

or

$$t = \frac{h}{H_0a},$$

which shows that the temperature indicated is proportional to the depression h of the mercury-column from the position occupied by it when the thermometer is at 0°, since the denominator H_0a of the expression for t is constant. This calculation, however, is only approximate, as the expansion of the bulb, the expulsion of some air from the bulb into the stem, and the effect of variation of temperature in the part of the stem dibaric periodate may be converted by ammonia, with separation of periodic acid, into the $\frac{2}{5}$-periodate $Ba^5I^4O^{19}$, or the $\frac{3}{8}$-periodate $Ba^8I^6O^{29}$; thus:

$$5Ba^2I^2O^9 + 5H^2O = 2Ba^5I^4O^{19} + 2H^5IO^6$$

and

$$4Ba^2I^2O^9 + 5H^2O = Ba^8I^6O^{29} + 2H^5IO^6.$$

The yellowish pentabaric salt which remains on treating with water the residue obtained by igniting the dibaric salt in a platinum crucible, dissolves easily in nitric acid, and this solution likewise yields with ammonia a precipitate of the $\frac{2}{5}$-periodate; thus:

$$2Ba^5I^2O^{12} + 5H^2O = Ba^5I^4O^{19} + 5BaH^2O^2.$$

Kämmerer, by mixing a hot aqueous solution of normal potassium periodate with a hot solution of barium nitrate, and adding potassium or sodium acetate after cooling, obtains an amorphous precipitate to which he assigns the composition $Ba^3H^3IO^6.KNO^3.HNO^3$. From a solution of this salt the barium is not precipitated by alkaline carbonates or sulphates; this reaction (with ammonium carbonate) affords a means of distinguishing periodic from iodic acid (*Zeitschr. f. Chem.* [2] v. 276).

Strontium Salts.—The *normal salt*, $SrI^2O^8 + 6H^2O$, crystallises from acid solution over sulphuric acid in transparent or milk-white, six-sided, often tabular prisms acuminated with three faces, and probably belonging to the triclinic system. The *distrontic salt* $Sr^2I^2O^9 + 4H^2O$ crystallises from a solution nearly neutralised with strontium carbonate, in crystalline crusts, mixed with the normal salt, which may be dissolved out by water. It gives off one-third of its water at 200° (Rammelsberg).

Calcium Salts.—The *normal salt*, CaI^2O^8, separates from a highly concentrated acid solution together with crystals of the acid. The *dicalcic salt*, $Ca^2I^2O^9 + 9H^2O$, is obtained by imperfectly saturating periodic acid with calcium carbonate, and evaporating over sulphuric acid, in soluble crystals which when heated above 100° give off their water, with partial decomposition. From the aqueous solution ammonia throws down a gelatinous precipitate of the salt $Ca^8I^6O^{29}$ (Rammelsberg).

Magnesium Salts.—A solution of magnesium carbonate in excess of periodic acid deposits first the *dimagnesic salt*, $Mg^2I^2O^9$, then the *normal salt*, $MgI^2O^8 + 10H^2O$, which dissolves in water with acid reaction. The dimagnesic salt is also produced by mixing the solutions of a magnesium salt and normal sodium periodate, and crystallises in small tabular rhombic prisms of 116°. When magnesium carbonate is digested with water and a slight excess of periodic acid, the *tetramagnesic salt*, $Mg^4I^2O^{11}$, separates as a crystalline powder; the same salt is obtained as an amorphous precipitate on saturating the mother-liquor of the preceding salt with sodium carbonate. It contains between 6 and 9 mol. water, effloresces over sulphuric acid, and partially also on exposure to the air. *Potassio-magnesic periodates* are obtained on adding magnesium sulphate to a solution of the potassium salt, $K^4I^2O^9 + 9H^2O$. The liquid then becomes acid, and a crystalline precipitate is formed, varying in composition according to the proportions and concentration of the solution, but apparently always consisting of the normal potassium salt and the tetramagnesic salt $Mg^4I^2O^{11}$. The reaction takes place in the manner shown by the equations:

$$K^4I^2O^9 + 2MgSO^4 = Mg^2I^2O^9 + 2K^2SO^4$$

$$Mg^2I^2O^9 + 2MgSO^4 + 2H^2O = Mg^4I^2O^{11} + 2H^2SO^4$$

$$K^4I^2O^9 + H^2SO^4 = 2KIO^4 + K^2SO^4 + H^2O.$$

Remmelsberg observed the salts

$$\left.\begin{matrix} Mg^4I^2O^{11} \\ 6KIO^4 \end{matrix}\right\} + 24H^2O, \qquad \left.\begin{matrix} Mg^4I^2O^{11} \\ 4KIO^4 \end{matrix}\right\} + 20H^2O, \qquad \left.\begin{matrix} Mg^4I^2O^{11} \\ 2KIO^4 \end{matrix}\right\} + 16H^2O.$$

When the magnesium sulphate is added in excess, the precipitate may also contain the salt $Mg^2I^2O^9$. *Ammonio-magnesic periodate*, $(NH^4)MgIO^5 + 3H^2O$, is precipitated by ammonia from a solution of the salt $Mg^2I^2O^9$ in nitric acid, as a finely crystalline precipitate which may be washed with cold water. The salt may be regarded either as $(NH^4)^4I^2O^9.Mg^4I^2O^{11} + 12H^2O$, or as $(NH^4)^3IO^5.Mg^3I^2O^{10} + 6H^2O$.

Zinc Salts.—The salt $Zn^2I^2O^9 + 6H^2O$ separates as a white powder on partially saturating a dilute solution of periodic acid with zinc oxide. The salt $Zn^5I^4O^{19} + 14H^2O$ is thrown down on adding normal sodium periodate to a solution of zinc-sulphate, as a pulverulent precipitate, in small quantity in the cold, more abundantly when the liquid is heated. The filtrate mixed with ammonia, not to saturation, yields an amorphous precipitate having the composition $Zn^9I^4O^{23} + 12H^2O$. *Zinco-potassic* *periodate*, $2KIO^4.Zn^4I^2O^{11} + 4H^2O$, is precipitated by tetrapotassic periodate from a solution of zinc sulphate; the acid filtrate contains zinc as well as periodic acid, and gradually deposits crystals of normal potassium periodate (Rammelsberg).

Nickel Salts.—Recently precipitated nickel carbonate dissolves in periodic acid, with green colour, and formation of peroxide, iodate, and insoluble basic periodate of nickel. The acid green solution evaporated at a very gentle heat, or over oil of vitriol, yields light green crystals (rectangular four-sided prisms with oblique end-faces) of the salt $Ni^7I^8O^{33}$ or $NiI^2O^8.3Ni^2I^2O^9$, with variable amount of water (49 to 63 mol.). It is insoluble in water, but blackens when heated with water, forming iodate and peroxide of nickel. The same compound is precipitated from the acid mother-liquor by incomplete saturation with ammonia (Rammelsberg).

Cobalt Salts.—Lautsch by treating dry tetrasodic periodate with excess of cobalt sulphate, or by evaporating a solution of the two salts to dryness, obtained a dark yellow-greenish powder, to which he assigns the composition $Co^7I^4O^{21} + 16H^2O$ or $7CoO.2I^2O^7 + 16H^2O$; he finds, however, that it gives off chlorine when dissolved in hydrochloric acid: hence it should contain a cobaltic compound. According to Rammelsberg, alkaline periodates produce in solutions of cobaltous salts a precipitate consisting of hydrated cobalt peroxide mixed with cobaltous iodate (part of the latter also remaining in solution); the same products are likewise formed when cobaltous carbonate is dissolved in periodic acid. Exactly similar results are obtained with manganous salts. Ferrous salts yield with alkaline periodates a brownish-yellow precipitate of ferrous iodate.

Ferric Periodate, $(Fe^4)^{xii}I^2O^{13} + 21H^2O$ or $2Fe^2O^3.I^2O^7 + 21H^2O$, is formed on adding tetrapotassic periodate to solutions of ferric salts, as a light brownish-yellow precipitate, which dries up to dark brown lumps having a shining fracture.

Cadmium Salts.—The normal salt, CdI^2O^8, is formed as a heavy white powder mixed with a small quantity of the following salt, on treating cadmium carbonate with a hot solution of periodic acid. If an insufficient quantity of the acid is used, the tetracadmic salt $Cd^4I^2O^{11} + 3H^2O$ is produced. The acid mother-liquor of these two salts yields by spontaneous evaporation, the salt $Cd^2I^2O^9 + 9H^2O$ in rectangular four-sided tables belonging to the rhombic system. It is insoluble in water, and is converted by boiling therewith into a yellowish powder. A fourth salt, $Cd^{10}I^6O^{31} + 15H^2O$, or perhaps $Cd^2I^2O^9.2Cd^4I^2O^{11} + 15H^2O$, is obtained as an insoluble white precipitate, on pouring cadmium sulphate into normal sodium periodate.

Copper Salts.—The *pentacupric salt*, $Cu^5I^2O^{12} + 5H^2O$, separates as a green powder on adding cupric carbonate to aqueous periodic acid: it gives off half its water at 200°. When a solution of cupric nitrate is mixed with normal potassium periodate, a green precipitate is formed at first, and the blue acid filtrate afterwards deposits the tetracupric salt, $Cu^4I^2O^{11} + 7H^2O$, in dark green microscopic crystals. A solution of recently precipitated cupric hydrate in periodic acid first deposits the pentacupric salt, and then, by spontaneous evaporation, the dicupric salt $Cu^2I^2O^9 + 6H^2O$, in dark green crystalline aggregates. A *potassio-cupric salt* of uncertain composition is formed as a bright green precipitate on mixing the solutions of cupric nitrate and tetrapotassic periodate (Rammelsberg). Lautsch obtained the salt $Cu^4H^2I^2O^{12}$ or $4CuO.I^2O^7 + H^2O$, as a green crystalline mass, by treating the dry sodium salt with aqueous cupric sulphate, or as a siskin-green powder, by mixing the solutions of cupric sulphate and tetrasodic periodate (whereby no precipitate is produced), evaporating to dryness, redissolving, again evaporating, and washing (Rammelsberg).

Lead Salt.—The lead periodate precipitated on mixing the solutions of normal sodium periodate and lead nitrate has the composition $Pb^3I^2O^{10} + 2H^2O$ established by Langlois. When heated with a solution of periodic acid, it acquires a yellowish-red colour without giving up any of its lead, and is afterwards insoluble in nitric acid (Rammelsberg).

Mercury Salts.—A slightly acidulated solution of mercurous nitrate forms with normal sodium periodate a precipitate of *octomercurous periodate*, $Hg^8I^2O^{11}$ or $4Hg^2O.I^2O^7$, having a fine yellow colour. It is anhydrous, soluble in nitric acid, and when heated is resolved without residue into yellow and red mercuric iodide, metallic mercury, and oxygen (Rammelsberg). A *decamercurous salt*, $Hg^{10}I^2O^{12}$ or $5Hg^2O.I^2O^7$, is obtained by precipitating the solution of the tetrasodic salt with mercurous nitrate, or by digesting the same sodium salt in the solid state with the mercurous solution, as a light yellow precipitate, affording a characteristic reaction of periodic acid; it becomes somewhat darker at 100°, dissolves in nitric acid, and likewise in hydrochloric acid, with evolution of iodine chloride. Hydrogen sulphide throws down mercury from these solutions, without previous separation of iodine. Stannous chloride converts the salt into green mercurous iodide (Lautsch). *Mercuric periodate*, $Hg^5I^2O^{12} = 5Hg''O.I^2O^7$, is prepared, similarly to the corresponding mercurous salt, with mercuric nitrate (not with the chloride). It is a red precipitate, easily soluble in hydrochloric acid, sparingly in nitric acid, and is precipitated from the latter solution both by dilution with water and by saturation with ammonia, but is redissolved by excess of ammonia (Lautsch; Rammelsberg).

IRIDIUM. W. v. Schneider (*Ann. Ch. Pharm. Suppl.* v. 261; *Jahresb.* 1867, p. 314) prepares pure iridium from the aqueous solution of impure potassium chloriridiate by a process founded on the observation of Bunsen, that iridium is much less easily reduced from the aqueous solution of its tetrachloride by hydrogen than the other platinum metals. The portion of platinum-ore insoluble in nitromuriatic acid is freed from osmium by heating it, mixed with sodium chloride, to low redness in a stream of chlorine; the remaining mixture of chlorides is triturated with the smallest possible quantity of water, and then washed on a filter; the solution thus obtained is treated with chlorine; and after addition of a little hydrochloric acid, agitated to saturation with pulverised potassium chloride. The resulting precipitate, after being washed with water and with a saturated solution of potassium chloride, consists of the nearly pure potassio-chlorides of iridium, ruthenium, and platinum. It is dissolved in a large quantity of boiling water; the solution is placed in a vessel closed with a perforated caoutchouc stopper; and hydrogen gas is passed into it for several days, till the platinum and ruthenium are wholly precipitated in the metallic state, which may be known by testing the remaining olive-green liquid with potash, whereupon it will first become colourless, and after some time blue or turbid. The hydrogen in the apparatus must then be expelled by a stream of carbon-dioxide (otherwise explosions will happen on opening the vessel, resulting from the action of the precipitated metals on the mixture of hydrogen and oxygen); and the solution, which contains the greater part of the iridium as trichloride, is subjected to continued treatment with hydrogen. The iridium is then precipitated on the surface of the liquid in large brittle laminæ having a metallic lustre.

Respecting Gibbs's methods of separating iridium from other platinum metals, founded on the reactions of the chlorides with potassium nitrite and with luteo-cobaltic chloride, see PLATINUM METALS.

Iridium Bromides (Birnbaum, *Ann. Ch. Pharm.* cxxxiii. 161).—These compounds are not obtained by boiling iridium with nitric and hydrobromic acids, or by passing bromine over a red-hot mixture of metallic iridium and sodium bromide. But when moist iridic hydrate is treated with hydrobromic acid, a blue solution is obtained, which becomes more stable when mixed with nitric acid, and leaves on evaporation a blue deliquescent crystalline mass, which, however, does not unite directly with other metallic bromides.

Potassium Bromiridiate, $2KBr.IrBr^4$, is obtained by mixing potassium bromide with iridium tetrachloride, or by treating ammonium chloriridiate (or better the sodium salt) with potassium bromide. It forms black-blue octohedrons, and decomposes when its solution is evaporated. With alkalis it yields first the tribromide, then the hydrated sesquioxide; with silver nitrate it forms a precipitate of silver bromiridite, $6AgBr.Ir^2Br^6$.

Ammonium Bromiridiate, $2NH^4Br.IrBr^4$, prepared from the chloriridiate and sodium bromide, resembles the potassium salt. The *sodium salt*, $2NaBr.IrBr^4$, is deliquescent and unstable.

The *tribromide*, $Ir^2Br^6 + 8H^2O$, is deposited in olive-green crystals on evaporating the aqueous solution of the tetrabromide (obtained by decomposing potassium bromiridiate with silicofluoric acid). It forms very stable double salts, which are produced from those of the tetrabromide by heating, or more quickly by the action of sulphurous or sulphydric acid. The *potassium salt* $6KBr.Ir^2Br^6 + 6H^2O$ crystallises in large, olive-green, four-sided needles, which, if an excess of sulphurous acid has been used in their preparation, are mixed with white crystals. The *sodium salt* $6NaBr.Ir^2Br^6 + 24H^2O$ crystallises in rhombohedrons; the *ammonium salt* $6NH^4Br.Ir^2Br^6 + H^2O$, in microscopic olive-green needles; on evaporating the aqueous solution of the tribromide, the compound $6HBr.Ir^2Br^6 + 6H^2O$ separates in blue needles, brown-red by transmitted light.

The *sulphites* of iridium obtained by Birnbaum are described under SULPHUROUS ACID (v. 546).

IRON. Pure iron, of silver-white colour and strong lustre, may be obtained by heating nitride of iron moderately (below the melting point of lead) in a stream of hydrogen. Iron thus obtained has a sp. gr. of 6·03, and is soft enough to be cut with a knife. It oxidises in the air more easily than ordinary iron, especially at high temperatures and in contact with moisture (Stahlschmidt, *Jahresb.* 1865, p. 255).

Troost (*Bull. Soc. Chim.* [2] ix. 250) prepares pure iron by fusing pig iron in a lime crucible by the oxyhydrogen flame, assisted towards the end of the process by a stream of oxygen to oxidise the foreign constituents. On removing the slag from the surface, the iron remains pure, and in the form of a fused mass. According to Matthiessen a. Szczeparowski (*Chem. News*, xviii. 114), iron cannot be obtained perfectly free from sulphur. The metal obtained by igniting ferric oxide or chloride purified as completely as possible, in a stream of hydrogen, or by electrolytic precipitation, or by igniting purified potassium ferrocyanide, always yielded distinct traces of hydrogen sulphide when dissolved in dilute hydrochloric acid.

On the absorption of gases by iron, and on its permeability by hydrogen at a red heat, see GASES (p. 634).

Reactions.—1. From experiments by Calvert (*Chem. News*, xxiii. 98), it appears that the rusting of iron is due, not to free oxygen or aqueous vapour of the air, but to carbonic acid. Iron does not rust in perfectly pure water. Caustic alkalis and alkaline carbonates prevent the oxidation. When a plate of iron half immersed in a weak alkaline solution is exposed to the air, not only the immersed, but also the projecting part, remains bright and unaltered for months.

2. Malleable iron (turnings or wire) is attacked by dilute *nitric acid* of sp. gr. 1·03 to 1·06, either with elimination of hydrogen and formation of ferrous salt, or with elimination of nitrogen dioxide and formation of ferric salt, or without any evolution of gas. Sometimes hydrogen is evolved at the beginning of the action, and nitrogen dioxide afterwards, in which case the solution contains both ferrous and ferric salt. Ammonium nitrate may be formed in either of these reactions, but always in small quantity; nitrites do not appear to be formed. The passivity of iron and steel produced by nitric acid of given specific gravity depends upon a particular temperature. With acid of sp. gr. 1·38, it is produced after a short time at 31°; if the initial temperature was 32°, the passive state is not developed. A colourless acid of sp. gr. 1·42 produces passivity at 55°, but not at 56°; in red fuming nitric acid of sp. gr. 1·42, iron remains passive at 82°, but dissolves at 83°. With cast iron the results are not equally definite (Ordway, *Sill. Am. J.* [2] xl. 316).

3. Iron heated to 200° in a sealed tube with aqueous *sulphurous acid* forms a solution of ferrous sulphite and hyposulphite, together with brass-yellow crusts of iron bisulphide; the latter compound is also formed in distinct microscopic crystals when ferric oxide or pounded basalt is heated in like manner with sulphurous acid (Geitner, *Ann. Ch. Pharm.* cxxix. 350).

4. For the reaction of iron with hydrogen dioxide, see p. 719.

5. Solutions of ferrous salts heated to 130°–140° in sealed tubes with *sodium hyposulphite* are completely decomposed, yielding ferrous sulphide, FeS, which does not oxidise in contact with the air, is not perceptibly decomposed by strong hydrochloric or dilute sulphuric acid, but is quickly oxidised by nitric acid. Strongly ignited ferric oxide heated to redness with excess of sodium hyposulphite, yields a black sulphide of iron soluble in hydrochloric acid (Gibbs, *Jahresb.* 1864, p. 183).

6. According to Natanson (*ibid.* 1864, p. 714; 1865, p. 716), the smallest trace of iron in the form of ferric salt may be detected by agitating the solution, mixed with recently prepared potassium sulphocyanate, and scarcely coloured thereby, with ether. The ether then dissolves the ferric sulphocyanate and becomes rose-red, or, with somewhat larger quantities of ferric salt, blood-red. According to Erlenmeyer, the purple-red colour of the ethereal solution is completely destroyed by a large quantity of potassium sulphocyanate or by potassium tartrate; in great part also by sodium acetate. The reaction cannot be applied to the detection of potassium sulphocyanate with ferric chloride, as the ether in this case [*i.e.* with excess of ferric chloride] does not become coloured (Natanson).

Volumetric Estimation.—Oudemans (*Zeitschr. anal. Chem.* vi. 129) gives the following method, founded on the observation that sodium hyposulphite gradually added to a ferric solution containing free hydrochloric acid decomposes it, with formation of tetrathionic acid, and without evolution of sulphurous oxide or separation of sulphur, according to the equation,

$$2Na^2S^2O^3 + Fe^2Cl^6 + 2HCl = 4NaCl + 2FeCl^2 + H^2S^4O^6.$$

The acid solution, free from ferrous salts and heated to 40°, is mixed with a few drops of solution of cupric sulphate, then with potassium sulphocyanate till a dark red colour is produced, and the standard solution of sodium hyposulphite is added till the liquid appears transparent and colourless. The cupric salt acts as a contact substance, accelerating the reduction of the ferric oxide.

Mohr (*Zeitschr. anal. Chem.* ii. 243) has modified the method depending upon the use of potassium iodide, starch solution, and sodium hyposulphite described a

p. 385, vol. iii., so far as to heat the ferric solution with potassium iodide in a closed vessel, add the starch-paste only after cooling, and then the standard solution of hyposulphite. This solution is most readily titrated by means of potassium dichromate, 20 c. c. of a solution of this salt (containing 4·919 grms. in a litre) being heated in a closed flask with hydrochloric acid and potassium iodide, and the liberated iodine determined by the hyposulphite solution previously brought to an equal volume.

Winkler (*Jahresb.* 1865, p. 717) estimates iron in a solution of ferric chloride by reduction with cuprous chloride, according to the equation

$$Fe^2Cl^6 + Cu^2Cl^2 = 2FeCl^2 + 2CuCl^2,$$

the end of the reduction being indicated by the disappearance of the red produced in the solution by a few drops of potassium sulphocyanate. According to Hoch a. Clemm (*ibid.* 1866, p. 803), this method does yield accurate results.

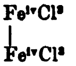
On the analysis of cast iron, see Tosh (*Chem. News*, xvi. 67, 94, 168); Mène (*Compt. rend.* lxviii. 449; *Zeitschr. f. Chem.* [2] v. 315). On the estimation of carbon in cast iron, see Elliot (*Chem. Soc. J.* [2] vii. 182); of sulphur, Eggertz (*Chem. News*, 1868, p. 207).

Compounds of Iron.

Iron belongs to the hexad group of metals, being bivalent in the ferrous, quadrivalent in the ferric salts, and sexvalent in the ferrates, its compounds being analogous to those of chromium:

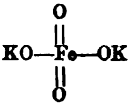
$Fe''Cl^2$

Ferrous chloride.



$$\begin{array}{c} Fe^{iv}Cl^3 \\ | \\ Fe^{iv}Cl^3 \end{array}$$

Ferric chloride.



$$\begin{array}{c} O \\ \| \\ KO—Fe—OK \\ \| \\ O \end{array}$$

Potassium ferrate.

Chlorides. *Ferrous chloride* is easily obtained well crystallised by heating sublimed ferric chloride in a stream of dry hydrogen (Wöhler, *Ann. Ch. Pharm. Suppl.* iv. 255).

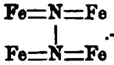
A compound of ferrous chloride with ethylene, $C^2H^4.FeCl^2$, is obtained by heating an ethereal solution of ferric chloride in a sealed tube for some hours to 140°–150°; more readily with addition of a small quantity of phosphorus dissolved in carbon bisulphide, in which case the heat of the water-bath is sufficient. It forms brittle, nearly colourless crystals, without lustre, easily soluble in water, moderately hygroscopic; they contain 2 mol. water of crystallisation. If the ether is quite anhydrous, the crystals are not formed. The recently prepared aqueous solution of the crystals exhibits the reactions of ferrous salts, and oxidises as readily as ferrous chloride (Kachler, *Deut. chem. Ges. Ber.* ii. 510; *Zeitschr. f. Chem.* [2] vi. 58).

Ferric Chloride.—The crystallised hexhydrated chloride, $Fe^2Cl^6.6H^2O$, melts, according to Ordway (*Sill. Am. J.* [2] xi. 329), at 31°; the decahydrate, $Fe^2Cl^6.12H^2O$, at 35·5°. Fresenius has shown (*Zeitschr. anal. Chem.* vi. 92) that ferric chloride is not volatilised from its solution mixed with hydrochloric acid, either by evaporation over the water-bath, or by tumultuous ebullition, or when the acid solution containing chlorides of alkali-metals is evaporated to dryness and heated for some time over the water-bath.

To prepare *basic ferric chloride* for medical purposes, Jeannel (*Compt. rend.* lxvi. 799) triturates 1,000 pts. of recently precipitated ferric hydrate free from sulphuric acid (containing 75 p. c. water), with 85 pts. hydrochloric acid of sp. gr. 1·2 and 500 pts. water, macerates for two days, and then filters. The above proportions correspond to the oxychloride $Fe^2Cl^6.9Fe^2O^3$. The dark garnet-red solution evaporated on plates at 50° leaves black scales which may be heated without alteration to 160°, become insoluble at 170°, and decompose at 220°. They are easily soluble in water, weak spirit, and glycerin. The solutions have an astringent, somewhat acid taste, are permanent, but yield precipitates with small quantities of sulphuric acid, sulphates, citric acid, tartaric acid, and even with a few drops of strong hydrochloric or nitric acid. They coagulate albumin, act as styptics in a higher degree than ferric chloride, and do not, like the latter, excite pain when applied to wounds. On the pharmaceutical preparation of ferric chloride, see also Attfield (*Pharm. J. Trans.* [2] vi. 396).

Fluoride. Ferric fluoride forms double salts with the fluorides of the alkali-metals. Berzelius obtained the potassium salts $2KF.Fe^2F^6$ and $4KF.Fe^2F^6$ (iii. 390).

Nicklès (*J. Pharm.* [4] vii. 15; *Jahresb.* 1868, p. 262) has obtained the ammonium salt $4NH^4F.Fe^2F^6$, and a sodium salt, both by direct combination and by decomposing the alkaline fluoride with a ferric salt. All these double fluorides crystallise readily, are sparingly soluble in water, and their solutions are decomposed by boiling, depositing yellow flocks. These solutions are not reddened by potassium sulphocyanate till the alkali-metal has been precipitated by means of an alcoholic solution of silicium fluoride.



Nitride. N^2Fe^4 or $\begin{array}{c}Fe{=}N{=}Fe\\ |\\ Fe{=}N{=}Fe\end{array}$.—This compound, analogous in composition to ammonium, is produced, according to Stahlschmidt (*Pogg. Ann.* cxxv. 37; *Jahresb.* 1865, p. 258), by the action of ammonia on metallic iron or ferric oxide. Sublimed ferrous chloride absorbs a considerable quantity of ammonia gas at ordinary temperatures, forming ferrammonium chloride, which when heated nearly to redness is converted into the nitride:

$$4FeCl^2 + 4NH^3 = N^2Fe^4 + 8HCl + 2H^2 + N^2.$$

The nitride thus obtained forms a grey powder or thin laminæ, sometimes also a compact very brittle silver-white mass, which may be rubbed to a very fine powder, burning with dazzling light when thrown into a flame. When moderately heated in hydrogen gas, it is reduced to pure iron, with formation of ammonia. Heated alone, or in a stream of nitrogen or ammonia, it gives off all its nitrogen, the last portions however with difficulty: hence the contradictory statements respecting its composition. Ignited in aqueous vapour it forms ammonia and ferroso-ferric oxide. It is slowly and imperfectly decomposed by boiling with water; dissolved by nitric acid with evolution of nitrogen dioxide, by dilute sulphuric or hydrochloric acid with evolution of hydrogen (but not of nitrogen, as stated by Despretz, iii. 391):

$$N^2Fe^4 + 10HCl = 4FeCl^2 + 2NH^4Cl + H^2.$$

Heated with chlorine, bromine, and iodine, in presence of water, it is decomposed, with evolution of hydrogen (and probably also of nitrogen) and formation of ammonia and a ferric salt. Stahlschmidt is of opinion that this compound sometimes exists irregularly diffused in steel, and attributes to its occurrence the contradictory statements respecting the presence of nitrogen in steel.

Oxides. When borax is saturated in the outer blowpipe-flame with ferric oxide till the bead acquires a blackish-green colour and exhibits a dull crystalline surface on cooling, and the bead is then dissolved in hot nitric acid, the ferric oxide remains in three- or six-sided, sometimes rhombic plates, appearing yellowish red or black according to their thickness. Ferroso-ferric oxide may also be obtained in the crystalline form by similar means (Chatelier, *Jahresb.* 1867, p. 10). According to Elsner (*ibid.* 1866, p. 35), ferric oxide is somewhat volatile at the heat of a porcelain furnace. Sidot (*Compt. rend.* lxvii. 175) has obtained an oxide exhibiting magnetic polarity by heating ferric oxide in an earthen tube placed in the magnetic meridian to a temperature not sufficient to fuse the oxide; also by placing iron-foil rolled up into a tube in a vertical position in a furnace, and heating it till it is completely oxidised.

When a solution of ferric chloride diluted till its colour is scarcely perceptible is heated to 27° and above, it again becomes strongly coloured, exhibiting the characteristic tint of basic ferric chloride. This change is not due to loss of hydrochloric acid, for it takes place even in closed vessels. The solution retains its colour on cooling, but its chemical properties are completely altered; with potassium ferrocyanide it yields only a pale blue precipitate instead of Prussian blue, and with sodium chloride when warmed a gelatinous precipitate of pure ferric hydrate, which if immediately washed dissolves in pure water, but loses its solubility if left for a day or two in contact with the saline solution. When the solution modified by a heat of about 70° is dialysed, hydrochloric acid free from iron passes through, and ferric oxide remains on the dialyser, soluble in water and in dilute hydrochloric acid, insoluble in saline solutions, and identical with Graham's colloïdal ferric oxide (iii. 718). When the dilute solution of ferric chloride is heated to 100°, the water being replaced as it evaporates, the soluble hydrate gradually passes into the modification discovered by Péan de St. Gilles (iii. 395), which is insoluble in dilute mineral acids and in most saline solutions, but forms with water a solution clear by transmitted, turbid by reflected light. This modification was obtained by St. Gilles by prolonged heating of ferric acetate, and by Scheurer-Kestner in like manner from the nitrate. All these ferric salts of monobasic acids therefore exhibit the same reaction, splitting up at first into acid and soluble oxide, which remain separate if much water is present, while the soluble oxide is afterwards converted into the meta-oxide of St. Gilles. The salts of bibasic acids, the sulphate for example, yield when heated only insoluble basic salts. Lastly, if the solution be heated to 250°-300°, at which temperature neither the colloïdal oxide nor the meta-oxide can exist, crystallised anhydrous ferric oxide is precipitated, as observed by Sénarmont. These observations explain the necessity of the precautions to be observed in the quantitative precipitation of iron with sodium acetate. The precipitate formed on heating is the colloïdal oxide, which is insoluble in the saline solution, but dissolves for the most part when washed with cold water, and must therefore be washed with solution of ammonium chloride or acetate (Debray, *Zeitschr. f. Chem.* [2] v. 290).

According to F. Muck (*Zeitschr. f. Chem.* [2] iv. 41), the ferric hydrates formed from ferrous hydrate or carbonate by atmospheric oxidation differ in their properties (though not in their amount of water) from those which are precipitated from ferric salts. The latter when recently precipitated are bulky and gelatinous, dry up with considerable diminution of bulk to brittle lumps having a shining fracture, and when heated to redness are converted, with incandescence, into hard, black, vitreous ferric oxide. The ferric hydrates formed from ferrous hydrate, on the other hand, are pulverulent, and dry up, without much diminution of volume, to friable lumps, which have no shining fracture, do not glow when heated, and leave a brown-red lustreless earthy oxide. When ferrous sulphate is precipitated at the boiling heat by sodium carbonate, with addition of hypochlorite (1 mol. NaClO and 2 mol. Na^2CO^3 to 2 mol. $FeSO^4$), the precipitate dried at 100° has the composition $Fe^2O^3.H^2O$ or $\left.\begin{matrix}(Fe^2)^{vi}\\H^2\end{matrix}\right\}O^4$. If the precipitation takes place in the cold (in which case the complete conversion into ferric oxide takes several hours) the amount of water in the precipitate dried at 100° corresponds to the formula $Fe^2O^3.2H^2O$. At intermediate temperatures hydrates of intermediate composition are obtained. The precipitates thrown down at the boiling heat exhibit peculiar changes of colour when ignited; at a red heat they leave brown ferric oxide, which at a higher temperature becomes light brick-red, and at a white heat, light ochre-yellow and gradually violet-red. In spite of their soft and friable consistency, these oxides do not differ in their specific gravity (5·19 to 5·21) from iron-glance. An oxide of this character cannot be prepared from ferric salts in the wet way, but it may be obtained by adding basic ferric sulphate (precipitated from solutions of ferrous sulphate in contact with the air) to fused potassium hydrate, and lixiviating the fused mass. Such a preparation dried at 100° exhibited approximately the composition $3Fe^2O^3.5H^2O$, and when ignited, was converted, without incandescence, into a light brick-red and ultimately yellow oxide. By continued fusion with potassium hydrate, the precipitate loses water, and then assumes a violet colour when ignited (Muck).

Respecting the reactions of ferroso-ferric hydrate with acids, see Lefort (*Zeitschr. f. Chem.* [2] vi. 607).

Phosphides. These compounds have been examined by Freese (*Pogg. Ann.* cxxxii. 225; *Jahresb.* 1867, p. 282), who finds that of all those which have been hitherto described, only three are really definite compounds, viz. Fe^3P^4, Fe^2P^2, and Fe^4P^2.

The phosphides of iron are non-magnetic and nearly, if not quite, infusible; a small addition of iron carbide, however, renders them more fusible than cast iron. They are not attacked by cold hydrochloric acid; are dissolved and completely oxidised by hot nitric or nitromuriatic acid, also by hot strong sulphuric acid, with evolution of sulphurous oxide, and formation of phosphoric acid and ferrous oxide; very slowly by boiling dilute hydrochloric acid, $\frac{3}{8}$ of the phosphorus passing into the solution as phosphoric acid, while $\frac{5}{8}$ are given off as phosphine: $16P + 15H^2O = 10PH^3 + 3P^2O^5$; the undissolved portion has the composition of the original substance. They are also slowly attacked by dilute sulphuric acid at the boiling heat, with evolution of phosphine.

1. The compound Fe^3P^4, which Rose obtained by heating iron pyrites in phosphine, may also be prepared:

a. By heating finely divided iron, anhydrous ferrous chloride, or magnetic pyrites in phosphine:

$$3FeCl^2 + 4PH^3 = Fe^3P^4 + 6HCl + 3H^2,$$
$$3Fe^8S^9 + 32PH^3 = 8Fe^3P^4 + 27H^2S + 21H^2;$$

also, mixed with ferric phosphate, by heating ferric oxide in phosphine as long as water continues to form. The pure phosphide, Fe^3P^4, forms a dark bluish-grey powder of sp. gr. 5·04. It is permanent in the air at ordinary temperatures, but burns when heated, giving off a fourth of its phosphorus and forming ferroso-ferric phosphate, $Fe^4P^4O^{15}$. Ignited in hydrogen or carbon monoxide, it gives off part of its phosphorus, and is apparently converted into Fe^2P^2; it is not altered by heating in carbon dioxide.

2. The compound Fe^2P^2 is formed: *α*. Very slowly, by heating ferrous sulphide in a stream of phosphine:

$$2FeS + 2PH^3 = Fe^2P^2 + 2H^2S + H^2.$$

β. By passing phosphorus vapour, carried forward by a stream of hydrogen, over red-hot ferric oxide, this oxide being first reduced by the hydrogen to metallic iron, which then unites with the phosphorus.—*γ*. By decomposing anhydrous ferric chloride with phosphine at a red heat:

$$Fe^2Cl^6 + 2PH^3 = Fe^2P^2 + 6HCl.$$

The product obtained by this last process is a black lamino-crystalline mass; the first two methods yield the compound as a bluish-grey powder of sp. gr. 5·21, very much like the preceding phosphide, but of lighter colour. When heated in the air, it burns brightly, without evolution of phosphorus, and likewise forms ferroso-ferric phosphate. It is not altered by ignition in hydrogen, but gives off part of its phosphorus when heated to redness in carbon monoxide.

3. The compound Fe^4P^2, which has been frequently obtained by different methods in an impure state and with various properties, may be prepared by mixing 3½ pts. anhydrous ferric phosphate with 1 pt. of lampblack in a Hessian crucible, covering the mixture with a layer of common salt, and heating it to whiteness for several hours. On exhausting the contents of the crucible with dilute hydrochloric acid, the phosphide Fe^4P^2 remains as a light grey, crystalline, non-magnetic powder, of sp. gr. 5·74, and resembling the preceding phosphides in its other physical characters. When ignited in hydrogen, carbon monoxide, or carbon dioxide, it retains its pulverulent form and undergoes no alteration; ignited in contact with the air, it burns brightly and melts to a bluish mass of ferric phosphate. To obtain this compound pure, it is necessary that the iron salt (ferrous or ferric) be in excess, to prevent the formation of carbide of iron, and that the air be excluded. As the phosphide Fe^4P^2 is not altered by ignition in carbon monoxide, whereas the phosphides Fe^2P^4 and Fe^2P^2 give up phosphorus, it is probable that the two latter are converted by prolonged ignition in carbon monoxide into the first. Freese is also of opinion that this compound is the only phosphide present in pig-iron.

Silicides. 1. By fusing a mixture of 60 grms. sodium silicofluoride, 20 sodium, 22 cast steel, and 60 zinc, with common salt in a blast-furnace, a brittle crystallo-laminar, perceptibly magnetic regulus is obtained, containing 10·1 p. c. silicon, having a sp. gr. of 7·018 at 17°, and not attacked by strong hydrochloric acid.—2. Sodio-ferrous chloride (obtained by melting 40 grm. iron, 150 sal-ammoniac, and 80 sodium chloride, 5 grm. silicium, and 25 grm. sodium), fused for 2½ hours with 25 grm. fluor-spar, yields a well-fused, white, brittle silicide of iron, Fe^2Si (20–29 p. c. silicon and 79·71 iron), having a sp. gr. of 6·611. On dissolving a considerable quantity of this compound in dilute hydrofluoric acid, there remained a crystalline residue, containing nearly equal parts of silicon and iron.—3. Sodio-ferrous chloride (prepared from 60 grm. iron), 60 grm. sodium silicofluoride, and 45 grm. sodium, heated together to the melting point of nickel, yielded about 9 grm. of a very brittle iron silicide imbedded in the slag; it contained 30·86 p. c. silicon and 69·14 iron, answering to the formula $Fe^{10}Si^{9}$, and was probably therefore a mixture of FeSi and Fe^2Si. It was but slightly magnetic, non-crystalline, and had a sp. gr. of 6·239 at 19° (Hahn, *Ann. Ch. Pharm.* cxxix. 57).

Sulphides. When dry hydrogen sulphide is passed over precipitated ferroso-ferric oxide heated to whiteness in a tube, the oxide is first converted into magnetic pyrites, Fe^3S^4, which at a very intense heat is partly reduced by monosulphide, FeS. The latter is found in the cooler part of the tube, in non-magnetic black to lemon-yellow six-sided prisms with double pyramids, belonging to the hexagonal system; the former in the part of the tube which has been strongly heated, as a greyish-yellow, metallically lustrous, strongly polar magnetic mass; it is decomposed by hydrochloric acid, with evolution of hydrogen sulphide and separation of sulphur (Sidot, *Compt. rend.* lxvi. 1257).

On the double sulphides of iron with potassium, sodium, and silver, see SULPHUR SALTS.

IRON, METALLURGY OF. So far as relates to the chemistry of this branch of industry, little advance has been made since the publication of the article in the Dictionary. In smelting iron ores, the attempt to realise still greater economy of fuel by the use of the hot blast has been continued with some further success, and, with the same object, useful experiments have been made in augmenting the height and capacity of blast furnaces; but the improvement thus attained has not involved any new chemical facts, and it has consisted chiefly in carrying out to a further extent the principles previously understood to obtain.

In the conversion of pig metal into malleable iron or steel, the practice of the method introduced by Bessemer has been largely extended; but otherwise there has been, as in iron smelting, an equal absence of any direct advance of a chemical nature. Apart from the multitude of merely speculative or supposititious inventions, there has been indeed only one suggested improvement in the manufacture of malleable iron and steel which could be regarded as novel and intelligible on chemical principles, while even that claims mention here more as a matter of history than otherwise, since it has not been found available in practice. The method referred to was introduced by Mr. Heaton, who claimed that it was applicable to the production of malleable iron and steel of good quality from the inferior brands of pig iron obtained by smelting ores containing phosphorus. This claim gave a special interest to the Heaton method, in consequence of the necessity of using pig iron practically free from phosphorus in making malleable iron by Bessemer's method, for that necessity had been found a very serious limitation to the applicability of the Bessemer method.

Heaton's method of decarburation consisted in bringing the melted pig iron in contact with nitrate of soda, mixed with sand and lime in such proportion as to mitigate the mechanical effect of the explosive decomposition of the nitrate on its coming in contact with the melted pig iron. The operation was performed in a cylindrical iron vessel lined with fire-clay, the mixture of nitrate, lime, and sand being retained at the bottom by a perforated plate of cast iron, while the melted metal was run into the converter.

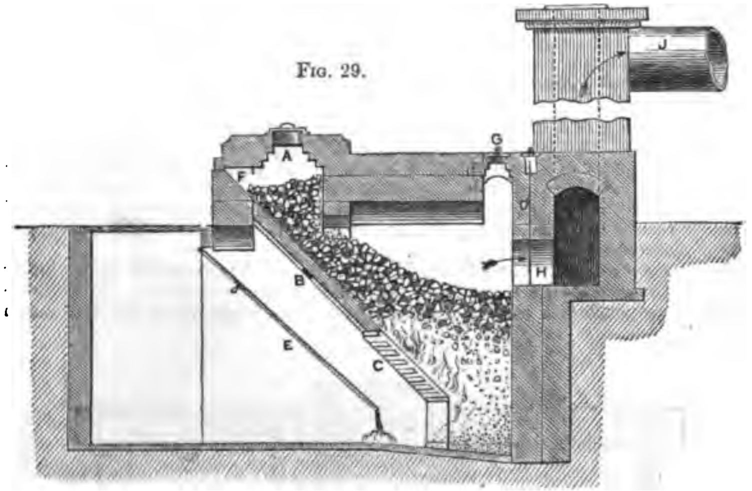
According to the description of the late Professor Miller, the reaction between the nitrate and the melted iron commenced in a very short time after the charge was run in, a moderate quantity of brown nitrous fumes escaped, and then there was a copious discharge of dark vapour, carrying out with it a portion of the liquid slag. After the lapse of five or six minutes there was a violent deflagration, attended with loud roaring noise and a burst of brilliant yellow flame, lasting for about a minute and a half. When that had subsided, the contents of the converter were emptied out on the ground, and the pasty mass of decarburetted metal was rendered compact and homogeneous by the usual operations of hammering and rolling.

The oxygen evolved from the nitrate of soda during its decomposition was undoubtedly the agent of decarburation, and probably the sodium of the nitrate operated at the same time in such a way as to separate sulphur and phosphorus from the iron. The exact nature of the reaction taking place has never been rendered evident, and though the experimental trials of the method left some uncertainty as to the extent to which phosphorus was separable in this way from pig iron, there was reason to believe that the treatment of pig iron in this way would be in any case too costly, by reason of the amount of nitrate required. Another, and at least equally serious objection to this method, as a means of making steel, arose from the condition in which the decarburised metal was left after the operation; for it may now be regarded as an axiom established by experience, that any method of producing steel, to be practically admissible, must ensure the perfect liquefaction of the metal during the decarburation, so as to give the highest degree of homogeneity, and must also yield the malleable metal in a liquid state, so as to afford the possibility of dealing with large masses of the melted metal, independent of the consumption of fuel hitherto needed for remelting.

It is in regard to this particular point that the chief recent advance has been made in the manufacture of malleable iron and steel. This has been done indirectly by means of the regenerative furnace introduced by Mr. C. W. Siemens, the principle of which is the gradual accumulation of the heat that would be wasted under ordinary conditions by passing off in the gaseous product of combustion. By this accumulation of heat within the furnace, a very much higher temperature may be attained than is possible with ordinary furnaces; it may also be maintained more easily and with a smaller consumption of fuel.

The fuel employed in the regenerative furnace introduced by Mr. Siemens is combustible gas produced by burning coal with a limited supply of air insufficient for perfect combustion. Any description of carbonaceous material may be worked in a suitable gas-producer, so as to furnish gas sufficiently good for the supply even of those furnaces in which the highest degree of heat is required. Coal is the fuel chiefly used for these gas furnaces in England; small coal has been employed in some cases, as in gasworks, where it is to be had at a cheap rate; wood is used in France, Bohemia, and Spain; sawdust in Sweden, furnishing gas for welding and other high-heat furnaces; lignite in various parts of Germany and Austria; peat in Italy and elsewhere. The gas-producer used for non-caking coal-slack consists of a rectangular fire-brick chamber, one side of which, as shown at B in the section, fig. 29, is inclined at an angle of from 45° to 60°, and provided with a fire-grate, C, at the lower part. The fuel is filled in at the top of this incline at A, so as to form a thick bed upon the grate. Air being admitted at the grate, the fuel is burnt immediately in contact with it to carbonic acid, but the gaseous product of combustion passes slowly upwards through the overlying red-hot fuel, while the carbonic acid it contains takes up an additional quantity of carbon, and is converted into carbonic oxide, while at the same time the gas becomes mixed with hydrocarbon gases and vapours distilled off from the raw fuel during its gradual descent along the inclined plane B towards the grate, The combustible gas thus produced is led off by a flue, H, into the furnace where it is to be burnt. Any ashes or clinkers that accumulate on the grate are removed at intervals of one or two days.

FIG. 29.



The composition of the gas varies with the nature of the fuel used and the arrangement of the gas-producer. At the Plate Glass Works of St. Gobain the gas obtained from a mixture of caking coal with one-third its weight of non-caking coal consisted of

	Volume		
Carbonic oxide	23·7	24·2	34·6
Hydrogen	8	8·2	
Carburetted hydrogen	2·2	2·2	
Carbonic acid	4·1	4·2	65·4
Nitrogen	61·5	61·2	
Oxygen	0·4		
	99·9	100	

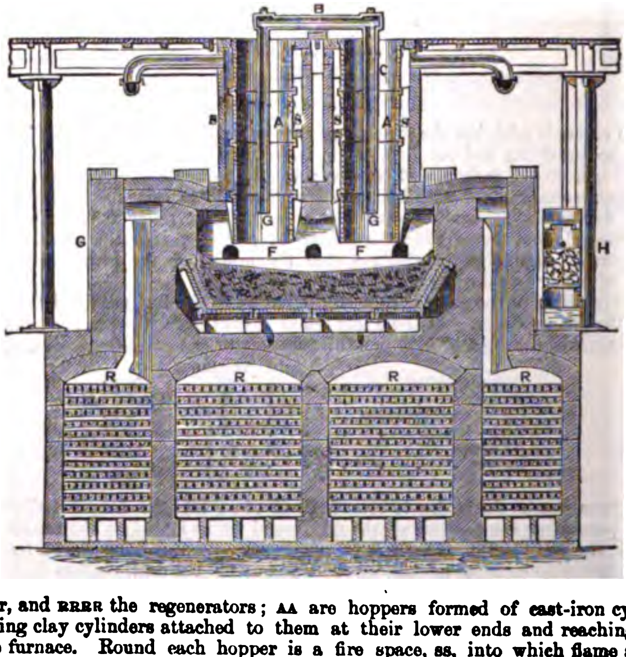
The oxygen was no doubt due to some leakage of air into the flue, and allowing for that, the percentage composition of the gas would be as stated in the second column of figures, the combustible constituents amounting to about 35 per cent. by volume. The presence of so large an amount of inert gas as 65 per cent. renders it difficult to maintain a high heat when gas of this description is burned in the ordinary way, but when the gas is burnt in a regenerative furnace that difficulty is overcome.

The principal feature of the regenerative furnace consists of four detached chambers situated beneath the furnace, and filled with fire-bricks stacked loosely together, so as to expose as much surface as possible. The chambers are made to communicate in pairs by means of flues, and these are fitted with valves in such a way that the hot waste gases from the flame may be made to pass from the furnace down through either pair of chambers at will. In this way the gaseous product of combustion, passing over surfaces successively cooler and cooler, gives up its heat to the layers of brick in the chambers, and at length escapes to the chimney nearly cold. The current of hot gas through one pair of chambers is kept up until the brickwork is uniformly heated to a considerable depth from the top, up to a temperature nearly equal to that of the gas entering them. Then by means of the valves the direction of the draught is changed, so that the hot gas passes down through the other pair of chambers, while at the same time the combustible gas supplied to the furnace, as well as the air required for burning it, are made to pass upwards through the heated pair of chambers, where, by contact with the brickwork, they become heated as they ascend. At some distance from the top the combustible gas and air thus attain a temperature nearly equal to the initial heat of the waste gases, and when they afterwards burn, on coming into contact in the furnace, the temperature produced by combustion is of course greater than if the gas and air had been supplied to the furnace at the ordinary temperature. By the time the temperature of the combustible gas and air begins to decrease the other pair of chambers will have been sufficiently heated, and the draught is to be again reversed, so as to make the combustible gas and air pass through the heated chambers, while the gaseous product of combustion passes through the cooled chambers.

By thus reversing the draught at regular intervals, nearly all the heat is retained in the furnace that would be otherwise carried off by the gaseous product of combustion. If the heat of the furnace be not abstracted continually by charging into it cold materials, the temperature will increase after each reversal of the draught, and by the gradual accumulation of heat in this way it is possible to obtain very high temperatures. But it is probable there must soon be a limit reached beyond which increase of temperature is impossible, for at a high temperature water vapour and probably carbonic acid are decomposed, and by that change a considerable quantity of heat is rendered latent.

With a regenerative furnace of this kind Mr. Siemens has succeeded in producing malleable iron and steel directly from the ore in a single operation. The furnace used for this purpose is shown in section by fig. 30, where FF is the combustion

FIG. 30.



chamber, and RRRR the regenerators; AA are hoppers formed of cast-iron cylinders supporting clay cylinders attached to them at their lower ends and reaching down into the furnace. Round each hopper is a fire space, SS, into which flame ascends from the furnace sufficiently to keep the hopper and its contents red hot. Each hopper has also a wrought-iron pipe, G, dipping down into it and connected with a main above, so that a current of ordinary combustible gas from the gas-producer may be forced in amongst the heated ore.

These hoppers are filled with iron ore, which is charged into them from above, after some charcoal has at first been introduced to form a basis for the ore in starting, and about half a ton of pig iron is placed upon the bed or hearth of the furnace through port-holes at the back or front. By the time the pig iron has melted, the ore in the lower part of the hoppers will have been reduced by the action of the gas, and the metallic sponge, sinking down into the bath of melted pig iron, is readily dissolved by it, thus making room for the upper portions of ore to sink down, become reduced and, in due course, dissolved in the bath of melted iron, fresh ore being continually supplied from above. This is continued until such time as the amount of carbon in the melted metal has been so far reduced as to correspond with the kind of steel required, and then the charge is run off into an ingot mould.

This kind of furnace has also been used for manufacturing steel from scrap iron and old malleable iron rails, the only difference in this case being that, in place of the vertical hoppers above described, the furnaces have slanting hoppers, through which the bars of iron are introduced, so that their ends rest in the bath of liquid metal, the bars sliding down as the metal is dissolved.

It is probable that in this operation the atmosphere of the furnace may itself contribute in part to the production of steel by direct carburation of the malleable iron, in consequence of its being free from the surplus oxygen present in an ordinary reverberatory puddling furnace, and being relatively much more highly carburetted. But, however this may be, there can be no doubt as to the practical advantage of the non-oxidising nature of the furnace atmosphere. In consequence of this, and of the small consumption of fuel, the charge of metal may be kept for some length of time in a melted state without suffering injury. The progress of the operation may be ascertained by removing from time to time a sample of the metal, and thus the character of the product may be regulated as required.

This method of producing steel, or that kind of steely iron which is now so much in demand for rails, has also a further advantage beyond effecting economy of fuel and admitting of old material being made serviceable again; for, while the ores from which rails are made generally contain too much phosphorus to admit of steel being made from them directly, the malleable iron obtained by puddling pig iron smelted from those ores is comparatively poor in phosphorus, the puddling operation being up to the present time the most effectual means of separating phosphorus and sulphur from iron. B. H. P.

ISATANE. $C^{32}H^{26}N^4O^6$.—This compound, which Laurent obtained by boiling disulphisatyde with acid ammonium sulphite (iii. 404), is likewise produced by the action of sodium-amalgam on isatin, in a solution kept acid by continual addition of sulphuric acid. It may be extracted by ether from the neutralised solution, and crystallises from ether or hot absolute alcohol in small white cubes insoluble in water. The alcoholic solution forms with ammoniacal silver nitrate a white precipitate of silver isatane, $C^{32}H^{22}Ag^4N^4O^6$. Heated with alcoholic potash to 130°, it forms potassium dioxindol and indiretin:

$$C^{32}H^{26}N^4O^6 + 2KHO = C^{16}H^{12}K^2N^2O^4 + C^{16}H^{16}N^2O^4$$

(Knop, *J. pr. Chem.* xcvii. 65).

ISATIC ACID. Syn. with TRIOXINDOL. (See INDOL, p. 734.)

The following salts of bromisatic acid have been examined by Gericke (*J. pr. Chem.* xcv. 176, 257):

Potassium salt,	$C^8H^5BrNO^3K$, easily soluble, cauliflower-like crystals.
Sodium salt,	$C^8H^5BrNO^3Na$, warty crystals.
Silver salt,	$C^8H^5BrNO^3Ag$, light yellow needles.
Barium salt,	$(C^8H^5BrNO^3)^2Ba$, sparingly soluble yellow crystals.
Copper salt,	$(C^8H^5BrNO^3)^2Cu + 2H^2O$, red granular precipitate.
Lead salt,	$(C^8H^5BrNO^3)^2Pb + 2H^2O$, scarlet crystalline precipitate.
Zinc salt,	$(C^8H^5BrNO^3)^2Zn + 2H^2O$, „ „ „

The potassium salt also forms yellow or brown precipitates with most other metallic salts.

ISATIN. $C^8H^5NO^2$.—On the preparation of isatin, see Gericke and Knop (*Jahresb.* 1865, p. 480). On the constitutional formula, see INDOL (p. 734).

Isatin suspended in water is converted by sodium-amalgam into dioxindol or hydrindic acid (p. 734). With tin and hydrochloric acid it forms indiretin, $C^{16}H^{16}N^2O^4$ (p. 728), together with another body which separates as a violet-red powder on evaporating the liquid filtered from the tin sulphide. This body heated to 180° is converted into a sublimate of yellow shining spangles, insoluble in alcohol, ether, and benzol, and not attacked even by concentrated acids and alkalis (Knop).

Isatin heated to 100° with hydriodic acid of sp. gr. 1·4 is converted, with separation of iodine, into isatyde, $C^{16}H^{12}N^2O^4$, and then at 140° into a dark green insoluble mass, which when freed from iodine by washing with sulphurous acid and with water, consists of three bodies. On treating this mass with boiling alcohol, a grey, nearly black residue, isatochlorin, is left, whilst a white and a red body pass into solution. On mixing the alcoholic solution with water, and treating the resulting precipitate, after drying, with ether, the white substance isatone remains undissolved, while the red substance isatopurpurin dissolves.

Isatochlorin, $C^{32}H^{24}N^4O^5$, is insoluble in alcohol, ether, and acetic acid, burns without melting on platinum foil, and dissolves when heated with tin and caustic soda, to a yellow liquid, from which hydrochloric acid throws down white flocks turning green on exposure to the air.

Isatone, $C^{32}H^{24}N^4O^8$, recrystallised from warm alcohol, forms yellowish-white slender needles, which melt when heated, and then carbonise without subliming.

Isatopurpurin, $C^{32}H^{25}N^4O^3$, obtained by evaporating the ethereal solution above mentioned, freed from a yellow substance by treatment with hot soda-ley, and recrystallised from glacial acetic acid, forms slender needles, dark red in the moist state, violet-red when dry. It is distinguished from indin (iii. 264) by its larger amount of carbon, and by its greater solubility in acetic acid and carbon bisulphide. Treated with tin and soda-ley, it dissolves, and the solution yields with hydrochloric acid a white precipitate which turns red in contact with the air (Schützenberger, *Bull. Soc. Chim.* [2] iv. 170).

An alcoholic solution of bromisatin heated with ammonia and evaporated, deposits bromimasatin, $C^{16}H^9Br^2N^3O^3$, in brownish-yellow crystalline masses or granules. On boiling bromisatin with strong alcoholic ammonia, and leaving the dark brown-red solution to evaporate, bromimesatin, $C^8H^5BrN^2O$, is deposited as a yellow-brown crystalline substance. Bromamasatin, $C^{32}H^{20}Br^4N^4O^7$ (?), is produced by evaporating an aqueous solution of ammonium bromisatate, and remains on treating the pasty residue with water, as an orange-yellow substance, slightly soluble in water, insoluble in alcohol and ether, but dissolving with violet colour in acids. Bromisamic acid, $C^{16}H^{11}Br^2N^3O^4$, separates from the potash-solution of bromamasatin, on neutralisation with dilute hydrochloric acid, as a powder of a fine red colour, nearly insoluble in water, but easily soluble in alcohol and ether. Its potassium salt, $C^{16}H^{10}Br^2N^3O^4K$, and its barium salt, $(C^{16}H^{10}Br^2N^3O^4)^2Ba$, crystallise in sparingly soluble yellow needles; the solution of the potassium salt gives yellow, brown, or bluish-red precipitates with most metallic salts. A hot alcoholic solution of bromisatin treated with hydrogen sulphide deposits a yellowish-white powder consisting of trisulphobromisatyde, $C^8H^5BrNO^{\frac{1}{2}}S^{\frac{3}{2}}$ (?), and disulphobromisatyde, C^8H^5BrNOS (Gericke, *J. pr. Chem.* xcv. 176, 257; *Jahresb.* 1865, p. 580).

Compounds of Isatin with Sulphites (H. Schiff, *Ann. Ch. Pharm.* cxliv. 45; *Zeitschr. f. Chem.* [2] iv. 13).—Laurent showed that isatin unites at the boiling heat with the acid sulphites of ammonium and potassium, forming compounds which he regarded as salts of a peculiar acid called *isato-sulphurous acid* (iii. 410). According to Schiff, these compounds are easily formed at ordinary temperatures, and are analogous in composition to the compounds of the aldehydes with alkaline bisulphites, so that the assumption of a peculiar isatosulphurous acid is unnecessary. Isatin, like the aldehydes, also combines directly with the acid sulphites of primary monamines.

Aniline salt, $C^8H^5NO^2.C^6H^7N.SH^2O^3$. On mixing the solutions of isatin in aqueous aniline and in aqueous sulphurous acid, the colour of the mixture immediately changes from orange-red to light straw-yellow, the liquid previously saturated with isatin becomes capable of taking up fresh quantities of it, and the solution yields on evaporation crystals of the compound of isatin with acid sulphite of aniline. This compound when separated from aqueous solution is always yellowish; from solution in ether it is obtained in white needles which shrink together considerably when pressed and dried. The corresponding *amylamine-compound* crystallised from ether has the composition $C^8H^5NO^2.C^5H^{13}N.SH^2O^3$, and is likewise easily soluble in water and in alcohol. Similar compounds are obtained with the sulphites of *ethylamine* and *toluidine*.

The preceding compounds are decomposed by acids, with separation of isatin; by alkalis with formation of isatates; hence in an acid or ammoniacal atmosphere they gradually assume a yellowish colour. The aniline-compound heated by itself first gives off sulphurous anhydride, then water, leaving a resinous mass which solidifies on cooling, and when several times recrystallised from ether-alcohol yields brownish crystals of phenylimesatin, $C^{14}H^{10}N^2O$:

$$C^8H^5NO^2.C^6H^7N.SH^2O^3 = SO^2 + 2H^2O + C^{14}H^{10}N^2O.$$

This latter compound, which contains the elements of isatin and aniline *minus* H^2O, was obtained by Engelhardt by the action of aniline on isatin in boiling alcoholic solution (iv. 485).

In like manner, amylimesatin, $C^{13}H^{16}N^2O = C^8H^5NO^2 + C^5H^{13}N - H^2O$, and that an indefinite number of different values might be found for the coefficient of expansion of the same substance, by measuring it in as many different directions. These different rates of expansion may however in all cases be referred to *three* principal rates of expansion in three directions at right angles to each other, so that the expansion in any given direction may be regarded as the resultant expansion due to three independent components, each of which takes part in the resultant expansion to an extent proportional to the length of the projection upon its own direction of a line parallel to the direction of the resultant expansion. Hence if a, a', and a'' are the three primary coefficients of expansion, the coefficient of expansion in any direction making the angles δ, δ', and δ'' respectively with the directions of the three primary directions of expansion may be represented by

$$D = a\cos^2\delta + a'\cos^2\delta' + a''\cos^2\delta'' \quad . \quad . \quad . \quad (1).$$

But, since the angles δ, δ', and δ'' are the angles made by the same straight line with three axes at right angles to each other, they fulfil the relation

$$\cos^2\delta + \cos^2\delta' + \cos^2\delta'' = 1 \quad . \quad . \quad . \quad . \quad (2).$$

In the case of *amorphous* substances, and those which crystallise in forms belonging to the *cubical* system, the three coefficients of expansion are equal, or $a = a' = a''$: hence formula (1) becomes $D = a(\cos^2\delta + \cos^2\delta' + \cos^2\delta'') = a$. That is to say, the expansion of such substances is the same in all directions.

In crystallised substances belonging to the *quadratic* and *hexagonal* systems, the coefficient of expansion has a special value corresponding to the direction of the principal crystallographic axis, but the coefficients for all directions equally inclined to the principal axis are the same. Hence the expansion of such crystals can be represented by making $a' = a''$ in formula (1), which then becomes $D = a\cos^2\delta + a'(\cos^2\delta' + \cos^2\delta'')$; or, since by formula (2) $\cos^2\delta' + \cos^2\delta'' = 1 - \cos^2\delta = \sin^2\delta$, the expansion may be expressed by $D = a\cos^2\delta + a'\sin^2\delta$. For all directions perpendicular to the axis, $\delta = 90°$, and consequently $\cos\delta = 0$, and $\sin\delta = 1$; hence for all such directions $D = a'$.

In crystals belonging to the *right prismatic system* the three principal axes of expansion are parallel to the crystallographic axes, but the coefficients of expansion corresponding to them are all unequal. The expansion of *monoclinic* crystals corresponds also to three unequal coefficients in directions at right angles to each other, but the relation between the positions of the crystallographic axes and those of the axes of expansion cannot be stated in general terms.

In all cases the coefficient of *cubical* expansion is equal to the sum of the three coefficients of linear expansion, or

$$a_c = a' + a + a'' \quad . \quad . \quad . \quad . \quad . \quad (3),$$

a relation which becomes $a_c = 3a$ when applied to amorphous substances or to crystals belonging to the regular system, and becomes $a_c = a + 2a'$ when applied to substances crystallised in forms belonging to the quadratic or hexagonal systems. In all cases also the coefficient of *mean linear* expansion is given by the expression

$$a_m = \tfrac{1}{3}(a + a' + a'') = \tfrac{1}{3}a_c.$$

The mean linear or the cubical expansion may thus be deduced from the measurement of one, two, or three coefficients of linear expansion, according to the crystalline system to which the substance belongs. It may however be obtained from a single measurement of the coefficient of expansion in a direction equally inclined to the three axes of expansion; for if in equation (1) we make $\delta = \delta' = \delta''$, we get $D = (a + a' + a'')\cos^2\delta$. But, under these conditions, equation (2) gives $\cos^2\delta = \tfrac{1}{3}$, or $\delta = 54° 44'$, and therefore $D = \tfrac{1}{3}(a + a' + a'') = a_m$.

In the following tables of results, the letters A, B, and C denote the coefficients of expansion parallel to the three principal axes of expansion respectively, M denotes the coefficient of mean linear expansion obtained by direct measurement in a direction inclined at 54° 44′ to the axes, and M_1 the same coefficient calculated by the formula $a_m = \tfrac{1}{3}(a + a' + a'')$, or when two coefficients are equal, $a_m = \tfrac{1}{3}(a + 2a')$. The numbers in the first table are given chiefly by way of illustration of the above-mentioned relations between expansion and crystalline form:

the *silver salt* is pasty and reducible by heat; the *lead salt* $C^8H^6PbO^3$ is a bulky precipitate, becoming crystallo-granular when heated with water.

ISOMERISM. On the simultaneous formation of isomeric bodies in definite proportions, see Rosenstiehl (*Compt. rend.* lxx. 260; *Zeitschr. f. Chem.* [2] vii. 249).

ISOMORIN. See Morin.

ISONITROPHENOL. See Phenol, Derivatives of.

ISO-OXYBUTYRIC ACID. See Isobutyric Acid, under Butyric Acid (p. 378).

ISOPHTHALIC ACID. See Phthalic Acid.

ISOPINIC ACID. See Opinic Acid.

ISOPROPACETIC ACID. See Valeric Acid.

ISOPROPACETONE. See Ketones.

ISOPROPYL-CARBYLAMINE. See Cyanides, Alcoholic (p. 550).

ISOPROPYL-COMPOUNDS. See Propyl-compounds.

ISOPYROMELLITIC ACID. See Mellitic Acid.

ISO-UVITIC ACID. $C^9H^8O^4$.—See Gamboge (p. 628).

ITABROMOPYROTARTARIC ACIDS. } See Pyrotartaric Acid.
ITACHLOROPYROTARTARIC ACIDS. }

ITACONIC ACID. $C^5H^6O^4$ or $CO^2H—CH^2—C—CH^2—CO^2H$ (see Acids, Organic, p. 48).—Wilm (*Ann. Ch. Pharm.* cxli. 28) prepares this acid by subjecting citric acid, previously dehydrated over the water-bath, to dry distillation, till the distillate exhibits a light brown colour, and heating this distillate, which is a concentrated solution of citraconic acid, to 120°–130° in sealed tubes, whereby it is quickly converted into itaconic acid. The contents of the tube solidify on cooling to a crystalline mass of itaconic acid, which separates from concentrated aqueous solution in rhombic octohedrons, aggregated into a hard crust.

Itaconic acid heated with aqueous hydrobromic, hydrochloric, and hydriodic acids, unites directly therewith, forming itamonobromopyrotartaric acid, $C^5H^7BrO^4$, and the corresponding acids $C^5H^7ClO^4$ and $C^5H^7IO^4$. With excess of hydriodic acid iodine is separated, and pyrotartaric acid, $C^5H^8O^4$, is produced. Itaconic acid treated with chlorine is converted into itadichloropyrotartaric acid, $C^5H^6Cl^2O^4$ (Swarts, *Bull. Soc. Chim.* [2] iv. 374; *Jahresb.* 1865, p. 392; 1866, p. 404). See Pyrotartaric Acid.

Paraconic Acid. $C^5H^6O^4$.—An acid isomeric with itaconic acid, produced by abstraction of HCl from itamonochloropyrotartaric acid. It is prepared by heating this chlorinated acid with water to 140° for several hours in a sealed tube—or better by boiling it for 48 hours in an open vessel—neutralising with calcium carbonate, precipitating the calcium salt of itamalic acid, formed at the same time, with alcohol, mixing the filtrate with ether, and decomposing the calcium paraconate thereby separated, with oxalic acid. A better mode of preparation is to boil the solution of itachloropyrotartaric acid with silver carbonate. The filtered liquid on cooling deposits hard shining crystals of silver paraconate, from which the acid may be separated by hydrogen sulphide.

Paraconic acid forms a crystalline mass resembling itamalic acid. It is very soluble in water and in alcohol, sparingly in ether; melts at about 70°; is converted by dry distillation into citraconic anhydride, $C^5H^4O^3$, and by hydrobromic acid into itamonobromopyrotartaric acid.

Paraconic acid is monobasic. The metallic paraconates have a great tendency to change into itamalates, the latter being formed indeed whenever paraconic acid is neutralised with a base. The paraconates are prepared by decomposing silver paraconate (obtained as above) with a metallic chloride, but even then the product is sometimes not a paraconate, but an itamalate. The most stable paraconates are the calcium and silver salts. The *calcium salt* $(C^5H^5O^4)^2Ca + 3H^2O$ is easily soluble, and crystallises in slender shining needles, which give up 1 mol. water on exposure to dry air, the other two at 120°. The *silver salt* $C^5H^5O^4Ag$ crystallises from hot water in stellate groups of needles, and when boiled with silver oxide is converted into itamalate. The *sodium salt* $C^5H^5O^4Na$, crystallises by evaporation in a vacuum in confused deliquescent needles; its solution becomes acid when heated, and then after neutralisation yields the gelatinous sodium salt of itamalic acid (Swarts, *Jahresb.* 1867, p. 474).

ITA-IODOPYROTARTARIC ACIDS. See Pyrotartaric Acid.

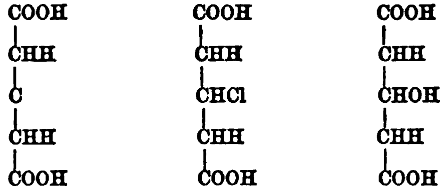
ITAMALIC ACID. $C^5H^8O^5$ (Swarts, *Bull. Acad. Belg.* [2] xxiv. 25; *Bull. Soc. Chim.* [2] ix. 317; *Laboratory*, p. 369).—This acid, homologous with malic acid, is produced by heating itamonochloropyrotartaric acid with bases, the change consisting in the replacement of the chlorine by hydroxyl:

$$C^5H^7ClO^4 + H^2O = C^5H^8O^5 + HCl.$$

When, however, water alone is used, paraconic acid is formed at the same time, which is difficult to separate. It is better, therefore, to boil the chlorinated acid in dilute solution with an alkaline carbonate till it is neutralised, then evaporate, saturate with hydrochloric acid, expel the excess of the latter by heating over the water-bath; extract the itamalic acid by means of ether free from alcohol; distil off the greater part of the ether; and crystallise the itamalic acid over sulphuric acid. A still better method is to heat a solution of the chlorinated acid with calcium carbonate as long as carbon dioxide continues to escape, then evaporate to a syrup, and add a large quantity of alcohol, which dissolves the calcium chloride, and throws down a gummy mass consisting of a soluble modification of itamalate. On decanting the alcoholic liquid, and heating this mass with a fresh portion of alcohol, it is transformed into a pulverulent insoluble precipitate, which is easily washed, and may then be suspended in water, and decomposed with a quantity of oxalic acid exactly sufficient to remove the calcium. The filtered solution may then be evaporated and left to crystallise over sulphuric acid.

Itamalic acid crystallises from a syrupy solution in long white interlaced needles. It is extremely soluble in water, and rapidly absorbs moisture from the air; dissolves also in alcohol and in ether; has a pleasant sour taste, but no smell. It melts at 60°–65°, and volatilises with vapour of water even at 100°. It is resolved by dry distillation into water and itaconic acid, $C^5H^6O^4$, which is partly converted by further dehydration into citraconic anhydride, $C^5H^4O^3$, just as malic acid, $C^4H^6O^5$, is resolved into water and fumaric acid, $C^4H^4O^4$, and converted by further dehydration into maleic anhydride, $C^4H^2O^3$.

The relation of itamalic acid to itaconic and itachloropyrotartaric acid is represented by the following formulæ:



$$\begin{array}{ccc}
COOH & COOH & COOH \\
\vert & \vert & \vert \\
CHH & CHH & CHH \\
\vert & \vert & \vert \\
C & CHCl & CHOH \\
\vert & \vert & \vert \\
CHH & CHH & CHH \\
\vert & \vert & \vert \\
COOH & COOH & COOH
\end{array}$$

Itaconic. Itachloro-pyrotartaric. Itamalic.

Itamalic acid is therefore triatomic and bibasic, and may be represented by the typical formula $\left.\begin{array}{c}H\\(C^5H^5O^2)''\\H^2\end{array}\right\}\begin{array}{l}O\\O^2\end{array}$. When heated in a sealed tube with hydrobromic acid, it gives up its alcoholic hydroxyl in exchange for bromine, and is converted into itamonobromopyrotartaric acid, $\left.\begin{array}{c}Br\\(C^5H^5O^2)''\\H^2\end{array}\right\}O^2$.

Itamalic acid forms both acid and neutral salts. The latter may be formed by double decomposition, when insoluble, or by decomposing itachloro- or itabromo-pyrotartaric acid with metallic hydrates or carbonates. They have a remarkable tendency to assume at first a pitchy or gummy state, but may be rendered pulverulent and crystalline by prolonged boiling with water. A neutralised solution of itamalic acid forms a brownish-red gelatinous precipitate with ferric salts; greenish-blue with cupric salts after some time or on boiling; white with lead nitrate (with the acetate only on addition of ammonia); and with silver nitrate a white gelatinous precipitate, soluble in boiling water, insoluble in a solution of silver nitrate, and deposited after prolonged boiling in the form of a crystalline powder. The acid itamalates may be obtained by the ordinary methods, or by heating the aqueous solutions of the paraconates:

$$\underset{\text{Paraconate.}}{C^5H^5M'O^4} + H^2O = \underset{\text{Acid Itamalate.}}{C^5H^6(M'H)O^5}$$

Sodium Itamalate, $C^5H^6Na^2O^5$, is obtained by boiling itachloropyrotartaric acid with sodium carbonate, and mixing the neutral solution with alcohol, as a syrupy liquid, which by prolonged boiling with water is converted into a crystalline mass. The acid *ammonium salt* $C^5H^7(NH^4)O^5.C^5H^8O^5$ remains on evaporating its solution over sulphuric acid, as a fibrous mass, separating from hot alcohol in small hexagonal tables like barium chloride. The *calcium salt* $C^5H^6CaO^5 + H^2O$, prepared as above described, forms a chalky powder more soluble in cold than in hot water, and converted by long contact with cold water into the gummy soluble modification. Nitric acid converts it, not into an acid salt, but into the trihydrated salt $C^5H^6CaO^5 + 3H^2O$, which separates in small hard crystals. The *lead salt* $C^5H^6PbO^5$, obtained by precipitation, forms a curdy mass which melts in hot water (like the malate), but loses this property after long boiling. The *silver salt* $C^5H^6Ag^2O^5$ is a gelatinous precipitate, probably containing 1 mol. water; it dissolves in hot water, and separates after prolonged boiling as a crystalline powder. The *copper salt* $C^5H^6CuO^4$ is precipitated slowly from hot solutions as a greenish-blue crystalline powder; by neutralising the free acid with cupric hydrate, the *basic salt* $2C^5H^6CuO^4.CuO$ is obtained. *Ethylic itamalate* is a colourless liquid having an agreeable peppery odour, but not distilling without decomposition.

ITATARTARIC ACID. $C^5H^8O^6$ (Wilm, *Ann. Ch. Pharm.* cxli. 28).—An acid produced by the action of hypochlorous acid upon itaconic acid. When a 1 p. c. solution of hypochlorous acid mixed with the levigated mercuric oxychloride formed in its preparation (p. 438) is gradually added to a solution of sodium itaconate containing not more than 2 p. c. of the salt, cooled by ice and excluded from light, the liquid in five or ten minutes loses the odour of hypochlorous acid and acquires an agreeable odour of chloroform. With more concentrated solutions the action is so violent that complete decomposition takes place, attended with evolution of carbon dioxide. The filtrate freed from mercury by hydrogen sulphide contains the additive product $C^5H^7ClO^5$ (which may be dissolved out by ether, but cannot be separated in the pure state), and on evaporating the solution, this compound is converted into itatartaric acid, as shown by the equation:

$$C^5H^7ClO^5 + H^2O = HCl + C^5H^8O^6.$$

To obtain the itatartaric acid, the liquid, freed from hydrochloric acid by repeated evaporation, is precipitated by lead acetate with addition of ammonia; the washed precipitate is decomposed by hydrogen sulphide; the filtrate is carefully concentrated, then freed from the rest of the chlorine by silver carbonate, and from silver by hydrogen sulphide, and left to evaporate in a vacuum. Or the residue, consisting of itatartrate and chloride of sodium, is mixed with the requisite quantity of sulphuric acid, and the acid extracted from the dried mass is purified by conversion into a lead salt.

Pure itatartaric acid is amorphous, vitreous, smells like honey when gently heated, deliquesces in the air, dissolves easily in alcohol, and does not volatilise perceptibly at 100° with aqueous vapour. The itamalates of the alkali-metals do not crystallise; they prevent the precipitation of ferric oxide and cupric oxide by alkalis. *Calcium itatartrate*, $C^5H^6CaO^6 + H^2O$ (?), forms crystalline masses sparingly soluble in water. The *barium salt* $C^5H^6BaO^6$ (at 100°) is amorphous, easily soluble in water, and precipitable therefrom by alcohol. The *copper* and *zinc salts* are amorphous and easily soluble. The *lead salt* $C^5H^6PbO^6$ is sparingly soluble in water, and crystallises from a mixture of the ammonium salt with lead acetate in highly lustrous monoclinic tabular crystals with truncated summits. The *silver salt* $C^5H^6Ag^2O^6$ is a bulky precipitate soluble in water, but not recrystallisable without decomposition.

Itatartaric acid is resolved by dry distillation between 125° and 170° into carbon dioxide, water, and pyro-itaracemic acid, $C^4H^6O^3$, which condenses in oily streaks in the neck of the retort:

$$C^5H^8O^6 = CO^2 + H^2O + C^4H^6O^3;$$

between 190° and 230° coloured empyreumatic products are formed. On evaporating the distillate over sulphuric acid in a vacuum, pyro-itaracemic acid remains as a mass having an acid odour, easily soluble in water and in alcohol, volatilising with vapour of water. Its salts do not crystallise. The *barium salt* $(C^4H^5O^3)^2Ba + H^2O$ (dried at 100°) is amorphous and glossy; the *lead salt*, which is likewise amorphous, is, after drying, sparingly soluble, but hygroscopic; the *silver salt* is soluble and very easily decomposible.

J

JADE. On the composition and localities of several varieties of this mineral, see Damour (*Compt. rend.* lvi. 861; lxi. 313, 357; *Jahresb.* 1865, p. 880).

JAROSITE. This mineral, from the Sierra Almagrera in Spain, has, according to Ferber (*Jahresb.* 1864, p. 860), the composition $K^2SO^4.5Fe^2O^3.SO^3 + 10aq$.

JASPER. An ochre-yellow jasper of sp. gr. 2·69 from Isle Royale in Lake Superior, has, according to Stieren (*Jahresb.* 1864, p. 848), the composition 67·33 p. c. SiO^2, 24·87 Al^2O^3, 1·68 MgO, 3·23 Fe^2O^3, 1·29 K^2O, and 1·58 water.

JEFFERISITE. This name is given by Brush (*Sill. Am. J.* [2] xli. 248) to the chloritic mineral from the serpentine of Westchester, Pennsylvania, formerly regarded by him as a variety of vermiculite (v. 997), but now recognised as a distinct species, inasmuch as it is optically biaxial. A similar mineral, also laminar and decrepitating, has lately been found in Japan, on the peninsula of Kadzusa, south of Yeddo.

JOLLYTE. A mineral related to hisingerite, from Bodenmais in Bavaria. It is compact, with flat-conchoïdal and splintery fracture, of dark brown colour, translucent with green or brown-red colour in thin splinters; powder leek-green to light greyish-green. Lustre faintly unctuous. Hardness = 3. Sp. gr. = 2·61. Melts with difficulty before the blowpipe, with slight intumescence, to a black slightly magnetic or non-magnetic mass. Gives by analysis 35·55 SiO^2, 27·77 Al^2O^3, 16·67 FeO, 6·66 MgO, and 13·18 water, corresponding with the formula $3(2FeO ; MgO.SiO^2).2(2Al^2O^3.SiO^2) + 12H^2O$ (v. Kobell, *J. pr. Chem.* xciv. 495).

JORDANITE. A rhombic sulphur-compound, not yet analysed, but probably a sulpharsenite, occurring, together with dufrenoysite (ii. 347), in the Binnenthal (G. v. Rath, *Pogg. Ann.* cxxii. 371; *Jahresb.* 1864, p. 827).

JUGLANS. The green shell of the walnut (*Juglans regia*) contains a yellow substance (*regianin*) which crystallises in elongated octohedrons or needles, dissolves easily in alcohol and in benzol, and changes in a few hours into an acid (*regianic acid*), $C^9H^{12}O^7$, which is black, amorphous, resinous, forms with alkalis soluble salts having a fine purple colour, and with lead oxide an insoluble brown-violet salt, $PbO.C^9H^{12}O^7$ (Phipson, *Compt. rend.* lxix. 1372). Regianin appears to be identical with Vogel a. Reischauer's *nucin* (iv. 143). The episperm of the nut contains a tannin. (See NUCITANNIN.)

K

KÆMMERERITE. J. B. Pearse (*Sill. Am. J.* [2] xxxvii. 211) has analysed three differently coloured varieties of this mineral from Lancaster County, Pennsylvania, in rhombic crystals of hardness 2·75, resembling many varieties of chlorite: A. pure green; sp. gr. 2·355; B. reddish-green; C. red; sp. gr. 2·383.

	SiO^2	Al^2O^3	Cr^2O^3	FeO	NiO	CaO	MgO	H^2O		
A.	28·622	18·375	1·967	3·734	0·370	1·446	32·125	14·025	=	100·664.
B.	31·857	13·746	2·154	2·370	0·215	1·273	34·901	13·982	=	100·498.
C.	31·315	12·840	2·985	2·475	0·450	0·815	35·020	13·200	=	99·100.

From these analyses, Pearse calculates, for the green variety the formula $2Al^2O^3.9MgO.5SiO^2 + 8H^2O$, and for the red and reddish-green varieties, which may be regarded as identical, the formula $2Al^2O^3.13MgO.7SiO^2 + 10H^2O$.

According to J. P. Cooke (*ibid.* xliv. 201), the crystals of kæmmererite are optically biaxial, exhibiting faint but distinct positive double refraction; they are also dichroïc, the crystals of the violet variety (violet chrome-chlorite) transmitting light with violet colour in the direction of the optic axis, while in all directions at right angles to this axis the ordinary ray is violet, the extraordinary ray hyacinth-red.

KAINITE (from *καινός*, new). A double salt, consisting mainly of potassium chloride and magnesium sulphate, occurring in the Leopold shaft of the Stassfurt salt-works. It forms a fine-grained mass of yellowish or grey colour; does not become moist in the air, but effloresces over sulphuric acid. According to Rammelsberg (*J. pr. Chem.* xcix. 63; *Jahresb.* 1867, p. 951), it consists of $KCl.MgSO^4 + 3H^2O$, about ⅛ of the potassium being replaced by sodium. The purer yellow variety gave by analysis 14·52 p. c. Cl, 13·54 K, 1·30 Na, 32·98 SO^3, 16·49 MgO, and 21·00 water. Its aqueous solution first deposits the known double salt $K^2Mg(SO^4)^2 + 6H^2O$; afterwards magnesium sulphate, $MgSO^4 + 7H^2O$, while the chlorides of magnesium and potassium remain in the mother-liquor. The magnesio-potassic sulphate is likewise precipitated from the solution of kainite by alcohol (Rammelsberg). See also Zincken and Reichardt (*Jahresb.* 1865, pp. 899, 900). According to Frank (*Jahresb.* 1868, p. 1019), kainite contains 36·34 K^2SO^4, 25·24 $MgSO^4$, 18·95 $MgCl^2$, and 19·47 H^2O, agreeing with the formula $K^2Mg(SO^4)^2.MgCl^2 + 6H^2O$.

KAOLIN, KAOLINITE. S. W. Johnson and J. M. Blake (*Sill. Am. J.* [2] xliii. 351, 405) propose the name *Kaolinite* for the minerals hitherto designated as phalerite, nacrite, lithomarge, and kaolin. They also describe a kaolinite occurring on Summit Hill, Pennsylvania, in small scaly crystals, and containing 45·93 p. c. SiO^2, 39·81 Al^2O^3, with traces of ferric oxide, and 14·02 water. For analysis of kaolin-earths from various localities, see L. Knaffl (*Dingl. pol. J.* clxxiv. 292; *Jahresb.* 1864, p. 846).

To distingush kaolin from common clay, Elsner (*Dingl.* clxxv. 85) agitates it in a test-tube with pure strong sulphuric acid, till a uniform mixture is produced; decants the acid after subsidence; dilutes it carefully with six volumes of water; and supersaturates the cooled solution with ammonia. Kaolin thus treated separates but slowly from the strong acid, and the diluted acid solution gives an immediate white precipitate with ammonia; whereas ordinary clay is but slightly attacked by the acid, separates quickly from it, and the acid after dilution gives but an insignificant precipitate with ammonia.

KEROLITE or **CEROLITE** (i. 836). An apple-green variety of this mineral, from Lake Itkul in the Ural, was found by R. Hermann (*J. pr. Chem.* xcv. 134) to contain 47·06 p. c. SiO^2, 31·81 MgO, 2·80 NiO, and 18·33 water.

KETONES. *Acetones* (Friedel, *Compt. rend.* xlv. 1013; xlvii. 552; lv. 53; *Ann. Ch. Pharm.* cxii. 236, 376. Freund, *Ann. Ch. Pharm.* cxviii. 1. Frankland a. Duppa, *Phil. Trans.* clvi. 37; *Chem. Soc. J.* [2] iv. 395; v. 102; *Jahresb.* 1865, p. 304; 1867, p. 394. Geuther, *Jahresb.* 1863, p. 323; 1865, p. 302. Wanklyn, *Chem. Soc. J.* [2] ii. 371; *Chem. News*, xviii. 121, 181; *Jahresb.* 1864, p. 461; 1868, p. 509).—Organic compounds consisting of carbon monoxide united with two alcohol-radicles; *e.g.*,

$$\text{Common Acetone, } CO\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right..$$

The two alcohol-radicles may be either similar, as in the example just given, or they may be dissimilar; *e.g.*,

$$\text{Methyl-ethyl Ketone, } CO\left\{\begin{matrix}C\,H^3\\C^2H^5\end{matrix}\right..$$

Sometimes the ketones are written as consisting of acid-forming radicle united with alcohol-radicle. This was the case in Gerhardt's *Traité de Chimie organique.* But, inasmuch as it has been shown that methyl-propionyl and acetyl-ethyl are identically the same things (see Popoff, *Jahresb.* 1867, p. 399), we are compelled to regard the distinction between the acid-forming and alcohol-radicle as lost in the production of the ketone. Moreover, ketones are actually generated by union between carbon monoxide and nascent alcohol-radicles; *e.g.*,

$$CO + 2NaC^2H^5 = Na^2 + CO(C^2H^5)^2.$$

The ketones form a very well-marked natural family, and exhibit the closest resemblance to one another. All the lower members of the family are thin colourless liquids, possessing a peculiar penetrating smell, which deserves to be called the ketone-smell. The lowest ketone, viz. common acetone, is soluble in water in all proportions; and all the ketones are perceptibly soluble in water, and likewise dissolve a certain quantity of water, which they retain with some degree of obstinacy. Ketones have little or no tendency to take up oxygen from the air, in this respect being different from aldehydes, which have this tendency, and are composed of carbon monoxide with one equivalent of alcohol-radicle and one equivalent of hydrogen; *e.g.*,

$$\text{Common Aldehyde, } CO\left\{\begin{matrix} CH^3 \\ H \end{matrix}\right. .$$

Ketones undergo very precise oxidation by treatment with a mixture of bichromate of potash and dilute sulphuric acid of a certain strength (viz. a solution containing 8 per cent. of the bichromate, and just enough sulphuric acid to form chrome-alum).

The products of oxidation by means of such a chrome-solution employed at temperatures not exceeding 100° are acids of the acetic series. A very simple law appears to govern the course taken by the oxidation, viz. that the carbon monoxide becomes attached to the lower of the two alcohol-radicles. Thus methyl-amyl ketone gives acetic and valerianic acids:

$$CO\left\{\begin{matrix} C\,H^3 \\ C^5H^{11} \end{matrix}\right. + O^3 = C^2H^4O^2 + C^5H^{10}O^2.$$

In accordance with this law, methyl-ethyl ketone gives only acetic acid, and not acetic and propionic acids:

$$CO\left\{\begin{matrix} C\,H^3 \\ C^2H^5 \end{matrix}\right. + O^3 = 2C^2H^4O^2.$$

In the instance of the simplest possible ketone, viz. dimethyl-ketone, which is common acetone, the products are acetic acid and formic acid, the latter, however, from its instability, rapidly passing into carbonic acid and water on prolonged oxidation:

$$CO\left\{\begin{matrix} CH^3 \\ CH^3 \end{matrix}\right. + O^4 = C^2H^4O^2 + CO^2 + H^2O.$$

In the instance of ketones containing any other normal alcohol-radicles, and even when the radicles are to some degree iso-compounds, the oxidation of the ketone by means of the above-mentioned chrome-solution is an operation yielding two atoms of acid with almost mathematical precision. When, however, the alcohol-radicles are in a marked degree iso-radicles, the oxidation becomes irregular. Thus, methyl-isopropyl ketone may be expected to give

$$CO\left\{\begin{matrix} CH^3 \\ CH(CH^3)^2 \end{matrix}\right. + O^6 = 2C^2H^4O^2 + CO^2 + H^2O.$$

Ketones can also take up hydrogen, and thereby pass into secondary alcohols; *e.g.*,

$$CO\left\{\begin{matrix} CH^3 \\ CH^3 \end{matrix}\right. + H^2 = C\left\{\begin{matrix} CH^3 \\ CH^3 \\ H \\ OH \end{matrix}\right.$$

This reaction is effected by the employment of sodium-amalgam in presence of water (Friedel).

Those ketones which contain methyl enter into combination with alkaline bisulphites, and form compounds which are often beautifully crystalline, and from which by distillation with a caustic alkali the ketone may be recovered in its original state. Ketones not containing methyl do not form compounds with alkaline bisulphites, or form them only with the utmost difficulty.

The ketones are produced in the following reactions:

1. By the action of carbon monoxide on the compounds of the alkali-metals: $CO + 2NaC^2H^5 = Na^2 + CO(C^2H^5)^2$ (Wanklyn).

2. By the action of the chloride of an acid-radicle on the zinc-compound of an alcohol radicle: $C^2H^3OCl + Zn(CH^3)^2 = C^2H^3O.CH^3 + ZnClCH^3$ (Pebal a. Freund).

3. By distillation of the baryta- or lime-salts of the fatty acids, this being the original process by which common acetone was first prepared:

$$\left.\begin{matrix} (COCH^3)^2 \\ Ba'' \end{matrix}\right\}O^2 = \left.\begin{matrix} CO \\ Ba'' \end{matrix}\right\}O^2 + CO(CH^3)^2.$$

If a mixture of the salts of two different fatty acids be employed, the product is a ketone containing different alcohol-radicles (Williamson):

The phenomena attending the vaporisation of liquids under very great pressure (already mentioned in vol. iii. pp. 95, 96) have been further investigated by Andrews (*Phil. Trans.* 1869, p. 575), for an account of whose results see the article CARBON OXIDES in this volume (p. 401).

Heat of Chemical Action. Numerous determinations of the heating effects of chemical action, especially in relation to the mutual action of acids and bases, have been made by Thomsen of Copenhagen (*Pogg. Ann.* cxxxviii. 65, 205, 495; cxxxix. 193; cxl. 88, 497; abstr. *Zeitschr. f. Chem.* 1870, p. 533). His principal results are contained in the tables given on this and the preceding page, the first of which gives the quantity of heat (in hundreds of gramme-degrees) produced by the action of 1 molecular proportion (in grammes) of each of the acids named upon *a* molecules of sodium-hydrate in aqueous solution; the second gives the quantity of heat (similarly expressed) which is produced by the action of 1 molecule of sodium-hydrate on *a* molecules of each acid, also in aqueous solution (200 molecules of water to 1 molecule of sodium-hydrate or of acid).

TABLE II.

1 *Molecule of Sodium hydrate; a molecules of Acid.*

Name of Acid	*a*					
	2	1	½	⅓	¼	⅙
1. *Monobasic acids*:						
Hydrochloric	137	137	68·5			
Hydrobromic	137	137	68·5			
Hydriodic	136	137	68·5			
Hydrosulphuric	77	77	39			
Hydrofluoric	160	163	82			
Hydrocyanic	28	28	14			
Nitric	136	137	68			
Hypophosphorous	154	152	76			
Metaphosphoric	142	144	—			
Formic	—	132	—			
Acetic	132	132	66			
2. *Bibasic acids*:						
Hydrofluosilicic	—	133	133	—	—	
Sulphuric	142	146	155	—	78	
Selenic	—	148	152	—	76	
Sulphurous	—	159	145	—	73	
Selenious	—	148	135	—	69	
Hyposulphuric	—	—	135	—	—	
Chromic	—	131	124	—	63	
Phosphorous	149	148	142	96	—	
Carbonic (aqueous solution)	—	110	101	—	51	
Boric	129	111	100	68	—	34
Silicic	65	43	26	—	13·5	—
Stannic	—	—	—	—	24	—
Oxalic	138	138	141	—	71	—
Succinic	—	124	121	—	61	—
Tartaric	—	124	127	86	—	—
3. *Tribasic acids*:						
Citric	—	124	125	127	—	69
Orthophosphoric	147	148	135	113	—	59
Arsenic	147	150	138	120	—	62
4. *Tetrabasic acid*:						
Pyrophosphoric	—	144	143	—	132	91

From these results Thomsen draws the following general conclusions:

a. When 1 molecule of an acid acts upon sodium hydrate in aqueous solution, the evolution of heat is very nearly proportional to the quantity of soda, until this amounts to 1, 2, 3, or 4 molecules according as the acid is monobasic, bibasic, tribasic, or tetrabasic respectively.

b. When 1 molecule of sodium hydrate acts upon an acid in aqueous solution, the evolution of heat is very nearly proportional to the quantity of acid, until this amounts

12. Methyl-isoamyl ketone	$CO\left\{\begin{matrix}CH^3\\CH^2C(CH^3)^3\end{matrix}\right.$
13. Methyl-isoamyl ketone	$CO\left\{\begin{matrix}CH^3\\CH\left\{\begin{matrix}CH^3\\CH^2CH^2CH^3\end{matrix}\right.\end{matrix}\right.$
14. Methyl-isoamyl ketone	$CO\left\{\begin{matrix}CH^3\\CH\left\{\begin{matrix}CH^3\\CH(CH^3)^2\end{matrix}\right.\end{matrix}\right.$
15. Methyl-isoamyl ketone	$CO\left\{\begin{matrix}CH^3\\CH\left\{\begin{matrix}CH^2CH^3\\CH^2CH^3\end{matrix}\right.\end{matrix}\right.$
16. Methyl-isoamyl ketone	$CO\left\{\begin{matrix}CH^3\\C\left\{\begin{matrix}(CH^3)^2\\CH^2CH^3\end{matrix}\right.\end{matrix}\right.$
17. Diethyl ketone	$CO\left\{\begin{matrix}CH^2CH^3\\CH^2CH^3\end{matrix}\right.$
18. Ethyl-propyl ketone	$CO\left\{\begin{matrix}C^2H^5\\CH^2CH^2CH^3\end{matrix}\right.$
19. Ethyl-isopropyl ketone	$CO\left\{\begin{matrix}C^2H^5\\CH(CH^3)^2\end{matrix}\right.$
20. Ethyl-butyl ketone	$CO\left\{\begin{matrix}C^2H^5\\CH^2CH^2CH^2CH^3\end{matrix}\right.$
21. Ethyl-isobutyl ketone	$CO\left\{\begin{matrix}C^2H^5\\CH^2CH(CH^3)^2\end{matrix}\right.$
22. Ethyl-isobutyl ketone	$CO\left\{\begin{matrix}C^2H^5\\CH\left\{\begin{matrix}CH^3\\CH^2CH^3\end{matrix}\right.\end{matrix}\right.$
23. Ethyl-isobutyl ketone	$CO\left\{\begin{matrix}C^2H^5\\C(CH^3)^3\end{matrix}\right.$
24. Ethyl-amyl ketone.	$CO\left\{\begin{matrix}C^2H^5\\CH^2CH^2CH^2CH^2CH^3\end{matrix}\right.$

&c. &c.

The methyl-ketones (1–16) form compounds with alkaline bisulphites, and yield acetic acid by 'limited' oxidation (p. 150). The ethyl-ketones (17–24) do not form compounds with alkaline bisulphites; they yield propionic acid by limited oxidation.

The modes of formation and principal properties of the methyl-ketones are as follows:

1. *Dimethyl Ketone.* $CO(CH^3)^2$.—Common acetone. Boils at 55·6°. Sp. gr. 0·7921 at 18°. Prepared: *a.* By dry distillation of barium or calcium acetate:

$$\left.\begin{matrix}(COCH^3)^2\\Ba\end{matrix}\right\}O^2 = \left.\begin{matrix}CO\\Ba\end{matrix}\right\}O^2 + CO\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right..$$

β. By the action of zinc-methyl on acetyl chloride (Pebal a. Freund):

$$Zn(CH^3)^2 + COCH^3Cl = Zn(CH^3)Cl + CO(CH^3)^2.$$

γ. By limited oxidation of dimethoxalic acid (Chapman a. Smith):

$$\left.\begin{matrix}C^2O(CH^3)^2\\H\end{matrix}\right\}O^3 + O = CO^2 + H^2O + CO(CH^3)^2.$$

δ. By the action of alkalis on acetate of acetylinated ethyl:

$$\left.\begin{matrix}C^2H^4(COCH^3)\\COCH^3\end{matrix}\right\}O + \left.\begin{matrix}Ba\\H^2\end{matrix}\right\}O^2 = C^2H^6O + \left.\begin{matrix}CO\\Ba\end{matrix}\right\}O^2 + CO\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right..$$

ε. By oxidation of isopropyl alcohol:

$$\left.\begin{matrix}CH(CH^3)^2\\H\end{matrix}\right\}O + O = H^2O + CO(CH^3)^2.$$

2. *Methyl-ethyl Ketone,* $C^4H^8O^2 = CO\left\{\begin{matrix}CH^3\\CH^2CH^3\end{matrix}\right.$; also *methylated acetone* (i. 31).—Boils at 81°; sp. gr. = 0·8125 at 13°. Obtained: *a.* By the action of zinc-ethyl on acetyl chloride:

$$Zn(C^2H^5)^2 + CO(CH^3)Cl = Zn(C^2H^5)Cl + CO(CH^3)(C^2H^5).$$

β. By the action of zinc-methyl on propionyl chloride:

$$Zn(CH^3)^2 + CO(C^2H^5)Cl = Zn(CH^3)Cl + CO(CH^3)(C^2H^5).$$

γ. By the action of alkalis on propionate of acetylinated ethyl:

$$\left.\begin{matrix}C^2H^4(COCH^3)\\ COC^2H^5\end{matrix}\right\}O + \left.\begin{matrix}Ba\\ H^2\end{matrix}\right\}O^2 = C^2H^6O + \left.\begin{matrix}CO\\ Ba\end{matrix}\right\}O^2 + CO\left\{\begin{matrix}CH^3\\ C^2H^5\end{matrix}\right..$$

3. *Methyl-propyl Ketone.* $CO\left\{\begin{matrix}CH^3\\ CH^2CH^2CH^3\end{matrix}\right.$—Boils at 101° (barometer 760 mm.). Sp. gr. at 13° = 0·8132; sp. gr. at 22° = 0·8046.

Discovered by Geuther; also described by Frankland a. Duppa as ethylacetone. Obtained by the action of butyrate of acetylinated ethyl on potash or baryta-water:

$$\left.\begin{matrix}C^2H^4(C^2H^3O)\\ {}^{*}C^4H^7O\end{matrix}\right\}O + \left.\begin{matrix}H^2\\ Ba\end{matrix}\right\}O^2 = C^2H^6O + CO\left\{\begin{matrix}CH^3\\ C^3H^7\end{matrix}\right. + \left.\begin{matrix}CO\\ Ba\end{matrix}\right\}O^2.$$

4. *Methyl-isopropyl Ketone.* $CO\left\{\begin{matrix}CH^3\\ CH(CH^3)^2\end{matrix}\right.$—Boils at 93·5°. Sp. gr. at 13° = 0·8099. Discovered by Geuther (described by Frankland a. Duppa as dimethylated acetone). Prepared by the action of isobutyrate of acetylinated ethyl on baryta-water:

$$\left.\begin{matrix}C^2H^4(C^2H^3O)\\ COCH(CH^3)^2\end{matrix}\right\}O + \left.\begin{matrix}H^2\\ Ba\end{matrix}\right\}O^2 = C^2H^6O + CO\left\{\begin{matrix}CH^3\\ CH(CH^3)^2\end{matrix}\right. + \left.\begin{matrix}CO\\ Ba\end{matrix}\right\}O^2.$$

The isobutyrate of acetylinated ethyl is produced by acting on acetate of ethylene-sodium with methyl-iodide.

5. *Methyl-butyl Ketone.* $CO\left\{\begin{matrix}CH^3\\ CH^2CH^2CH^2CH^3\end{matrix}\right.$—Obtained by the action of chloride of valeryl on zinc-methyl.

6. *Methyl-isobutyl Ketone.* $C^6H^{12}O = CO\left\{\begin{matrix}CH^3\\ CH^2CH(CH^3)^2\end{matrix}\right.$—The *isapropacetone* of Frankland a. Duppa. The ketone obtained by oxidising β hexylic alcohol from mannite appears to have this constitution. It boils at 127° C. Sp. gr. 0·8298 at 0° (Wanklyn a. Erlenmeyer). By oxidation it gives acetic and isobutyric acids. It forms crystalline compounds with alkaline bisulphites. It is also produced by the action of alkalis on isovalerate of acetylinated ethyl:

$$\left.\begin{matrix}C^2H^4C^2H^3O\\ COCH^2CH(CH^3)^2\end{matrix}\right\} + \left.\begin{matrix}H^2\\ Ba\end{matrix}\right\}O^2 = C^2H^6O + CO\left\{\begin{matrix}CH^3\\ CH^2CH(CH^3)^2\end{matrix}\right. + \left.\begin{matrix}CO\\ Ba\end{matrix}\right\}O^2.$$

Isovalerate of acetylinated ethyl was obtained by Frankland a. Duppa by the action of isopropyl iodide on sodium-triacetyl, and designated by them as isopropacetone-carbonate.

7. *Methyl-isobutyl Ketone.* $CO\left\{\begin{matrix}CH\\ CH\end{matrix}\right.\left\{\begin{matrix}CH^3\\ CH^2CH^3\end{matrix}\right.$.—It appears to be unknown. Theory, however, indicates that it should be formed similarly to the ketone just described, viz. from the isovalerate of acetylinated ethyl which is obtainable by acting with mixed iodide of methyl and iodide of ethyl on acetate of ethylene-sodium.

8. *Methyl-isobutyl Ketone.* $CO\left\{\begin{matrix}CH^3\\ C(CH^3)^3\end{matrix}\right.$.—Unknown.

15. *Methyl-isoamyl Ketone.* $CO\left\{\begin{matrix}CH^3\\ CH(C^2H^5)^2\end{matrix}\right.$.—Boils at 137·5° to 139°. Sp. gr. at 22° = 0·8171. Discovered by Frankland a. Duppa, and named by them diethylated acetone. Prepared by the action of caproate of acetylinated ethyl on hydrate of barium:

$$\left.\begin{matrix}C^2H^4(C^2H^3O)\\ C^6H^{11}O\end{matrix}\right\}O + \left.\begin{matrix}H^2\\ Ba''\end{matrix}\right\}O^2 = C^2H^6O + CO\left\{\begin{matrix}CH^3\\ C^6H^{11}\end{matrix}\right. + \left.\begin{matrix}CO\\ Ba\end{matrix}\right\}O^2.$$

The caproyl was diethylated acetyl, $CO.CH(C^2H^5)^2$, and therefore the resulting amyl was diethylated amyl. The caproate of acetylinated ethyl was obtained by the action of iodide of ethyl on acetate of ethylene-sodium. J. A. W.

KRYPTOPHANIC ACID. Syn. with CRYPTOPHANIC ACID.

KUBA WOOD, the best kind of fustic, from *Morus tinctoria*, contains a substance which exhibits the kind of fluorescence observed by Hlasiwetz a. Pfaundler in isomorin.

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* The butyryl was normal butyryl, obtained by the action of ethyl iodide on sodium triacetyl.

The alcoholic solution of the aqueous extract of kuba wood is dark garnet-red by transmitted light, and fluorescent, with dark green colour, by reflected light. After being considerably diluted with alcohol, and then mixed with alum or any other aluminium salt, it exhibits a fluorescence similar to that of uranium glass, which disappears on addition of excess of alkali or hydrochloric acid, but reappears on exact neutralisation. The solution of the extract in ether, amylic alcohol, or methylic alcohol exhibits similar properties (Goppelsröder, *Pogg. Ann.* cxxxi. 464).

KUPFFERITE. An emerald-green variety of hornblende, allied to actinolite, occurring imbedded in the coarse-grained calcspar in the country of the Uralian Cossacks; also, imbedded in garnet, in the Ilmen mountains. It forms prismatic crystals ($\infty P : \infty P = 124° 15'$), cleaving parallel to ∞P, transparent in thin splinters, with glassy lustre; hardness = 5·5; sp. gr. = 3·08. Crystals from the Ilmen mountains gave by analysis:

SiO^2	Cr^2O^3	NiO	FeO	CaO	MgO	Alkalis	Loss by ignition	
57·46	1·21	0·65	6·05	2·93	30·88	trace	0·82	= 100

(R. Hermann, *Jahresb.* 1862, p. 726; Kokscharow, *ibid.* 1866, p. 927).

KUPHANILINE. A name applied by Reimann to the aniline oil obtained from that portion of crude benzol which boils at temperatures not above 100°. It contains 90 p. c. aniline and 5 p. c. toluidine, and distils at 100°–150° (*Dingl. pol. J.* clxxxv. 49; *Jahresb.* 1867, p. 460).

KYAPHENINE. Syn. with CYAPHENINE (p. 539).

KYNURENIC ACID. According to Voit a. Richter (*Jahresb.* 1865, p. 676), the quantity of this acid in dogs' urine increases when fat or carbohydrates are added to the food. Sodium sulphate, on the other hand, has no influence in this respect, contrary to the statement of Seegen (*ibid.* 1864, p. 650).

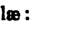
Kynurenic acid does not decompose barium carbonate. Its barium salt has a neutral reaction, is not decomposed by carbonic acid, but is precipitated thereby, together with barium carbonate, from the strongly alkaline solution. If after the passage of the carbonic acid gas, the liquid be heated to boiling, the neutral barium salt separates on cooling in stellate groups of needles, and the remaining liquid is found to be free from kynurenic acid (Liebig, *Ann. Ch. Pharm.* cxl. 143).

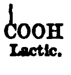
L

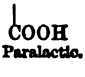
LABURNINE. A poisonous alkaloïd, occurring, together with cytisine, in the unripe seeds of the common laburnum (p. 539).

LACTALBUMIN and **LACTOPROTEÏN.** Two albuminous substances, occurring, according to Commaille (*J. Pharm.* [4] iv. 108), in milk together with caseïn.

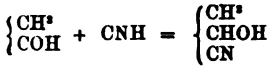
LACTAMIDE. According to Wislicenus (*Ann. Ch. Pharm.* cxxxiii. 257), the only products obtained by the action of dry ammonia gas on dilactic acid, $C^6H^{10}O^5$, are ammonium lactate and lactamide, $C^3H^7NO^2$. Laurent's lactamic acid (iii. 451) has no existence.

LACTIC ACID. $C^3H^6O^3$ =  $\begin{array}{l} C^2H^4OH \\ | \\ COOH \end{array}$.—The structure of the two modifications of this acid, known as ordinary or fermentation lactic acid, and paralactic acid, is represented by the following formulæ:

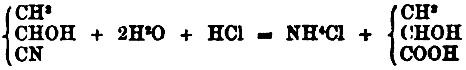

$$\begin{array}{l} CH^3 \\ | \\ CHOH \\ | \\ COOH \end{array}$$
Lactic.


$$\begin{array}{l} CH^2OH \\ | \\ CH^2 \\ | \\ COOH \end{array}$$
Paralactic.

Ordinary lactic acid, which may be supposed to contain the radicle ethylidene, $CH^3—CH$, is produced: *a*. By the oxidation of propylene glycol, $CH^3—CHOH—C^2H^2OH$ (iii. 454).—*β*. By the action of water and silver oxide on *a*-bromopropionic acid, $CH^3—CHBr—CO^2H$ (Friedel a. Machuca, iii. 454; Buff, *Ann. Ch. Pharm.* cxl. 156).—*γ*. By the action of hydrochloric acid on a mixture or compound of aldehyde and hydrocyanic acid (Wislicenus, *Ann. Ch. Pharm.* cxxviii. 1; Simpson a. Gautier, *ibid.* cxlvi. 254):

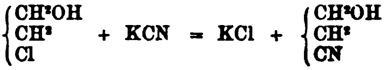


$$\left\{\begin{array}{l}CH^3\\COH\end{array}\right. + CNH = \left\{\begin{array}{l}CH^3\\CHOH\\CN\end{array}\right.$$

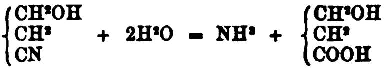


$$\left\{\begin{array}{l}CH^3\\CHOH\\CN\end{array}\right. + 2H^2O + HCl = NH^4Cl + \left\{\begin{array}{l}CH^3\\CHOH\\COOH\end{array}\right.$$

Paralactic acid, which is an ethylene compound, is formed: *a*. By heating ethylene chlorohydrate (glycolic chlorhydrin) with an alcoholic solution of potassium cyanide, and boiling the resulting ethylene cyanohydrate with potash (Wislicenus, *loc. cit.*):

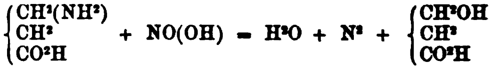


$$\left\{\begin{array}{l}CH^2OH\\CH^2\\Cl\end{array}\right. + KCN = KCl + \left\{\begin{array}{l}CH^2OH\\CH^2\\CN\end{array}\right.$$



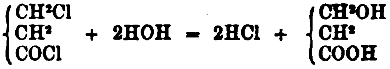
$$\left\{\begin{array}{l}CH^2OH\\CH^2\\CN\end{array}\right. + 2H^2O = NH^3 + \left\{\begin{array}{l}CH^2OH\\CH^2\\COOH\end{array}\right.$$

β. By the action of nitrous acid upon alanine (amidopropionic acid) (Buff, *Ann. Ch. Pharm.* cxl. 156):



$$\left\{\begin{array}{l}CH^2(NH^2)\\CH^2\\CO^2H\end{array}\right. + NO(OH) = H^2O + N^2 + \left\{\begin{array}{l}CH^2OH\\CH^2\\CO^2H\end{array}\right.$$

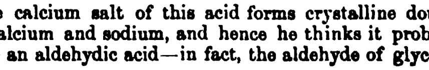
γ. By combining ethylene with carbonyl chloride, whereby paralactyl chloride, $CH^2Cl—CH^2—COCl$, is produced, and decomposing this chloride with an alkali:



$$\left\{\begin{array}{l}CH^2Cl\\CH^2\\COCl\end{array}\right. + 2HOH = 2HCl + \left\{\begin{array}{l}CH^2OH\\CH^2\\COOH\end{array}\right.$$

δ. By the action of silver oxide and water on *β*-iodopropionic acid, $CH^2I—CH^2—COOH$, produced by treating glyceric acid with iodine and phosphorus. Part of the paralactic acid is, however, converted by molecular transformation into ordinary lactic acid (Wichelhaus, *Ann. Ch. Pharm.* cxliv. 51; *Jahresb.* 1867, p. 402).

Beilstein (*Ann. Ch. Pharm.* cxxii. 369), by treating *β*-iodopropionic acid with recently precipitated silver oxide, obtained a tribasic acid, $C^{12}H^{22}O^{11}$, which he named hydracrylic acid. Moldenhauer (*ibid.* cxxxi. 330), by boiling this acid with silver oxide or alkalis, or by treating it with sodium-amalgam, obtained an acid having the composition of lactic acid; and this observation is confirmed by Wislicenus (*Zeitschr. f. Chem.* [2] iv. 684), who has moreover shown that the so-called hydracrylic acid, when simply neutralised with soda, likewise yields a sodium salt of lactic acid: hence he infers that the supposed hydracrylic acid has no existence, but that the acid formed by the action of moist silver oxide on *β*-iodopropionic acid is one of the modifications of lactic acid. Hydracrylic acid may, however, be an anhydride of lactic acid, $4C^3H^6O^3 - H^2O = C^{12}H^{22}O^{11}$, and may be converted into lactic acid by the action of alkalis. Socoloff (*ibid.* v. 123), by treating *β*-iodopropionic acid with moist silver oxide, likewise obtains an acid of the composition $C^3H^6O^3$; but on account [illegible] certain peculiarities in the characters of the zinc, calcium, and barium salts, he regards this acid as different from either of the known modifications of lactic acid. He finds, moreover, that the calcium salt of this acid forms crystalline double salts with the acid sulphites of calcium and sodium, and hence he thinks it probable that the acid in question may be an aldehydic acid—in fact, the aldehyde of glyceric acid:

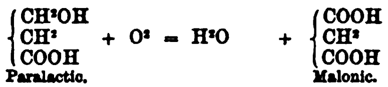


$$\left\{\begin{array}{l}CH^2OH\\CHOH\\CH^2OH\end{array}\right. \qquad \left\{\begin{array}{l}H^2OH\\HOH\\OH\end{array}\right. \qquad \left\{\begin{array}{l}CH^2OH\\CHOH\\COOH\end{array}\right.$$

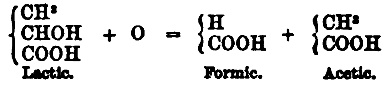
Glycerin. Glyceraldehydic acid. Glyceric acid.

It is difficult, however, to imagine how *β*-iodopropionic acid, $CH^2I—CH^2—CO^2H$, can give rise, by substitution of OH for I, to anything but paralactic acid. Moreover, Wislicenus (*ibid.* vi. 159) points out that the acid in question yields by oxidation, not glyceric, but (as first product) carbacetoxylic acid; that it is not converted into glycerin by nascent hydrogen; and when treated with hydriodic acid is easily transformed into β-iodopropionic acid. Sarcolactic acid appears to be a mixture of two acids, inasmuch as its zinc salt may be separated, by treatment with strong alcohol, into a sparingly soluble crystalline salt and an easily soluble amorphous salt. The acid of the latter appears to be identical with paralactic or β-oxypropionic acid; but that of the crystalline zinc salt is not identical with ordinary lactic acid, inasmuch as it exerts a strong dextrorotatory action on polarised light, whereas both ordinary lactic and paralactic acids are optically inactive. See further Heintz, *Ann. Ch. Pharm.* clvii. 291, 295;—Erlenmeyer, *ibid.* clviii. 262; also *Chem. Soc. J.* [2] ix. 361, 546.

Reactions.—1. Paralactic acid oxidised with *potassium dichromate*, or with dilute *nitric acid*, or by fusion with *potash*, is converted into malonic acid, $C^3H^4O^4$; but ordinary lactic acid treated with sulphuric acid and potassium dichromate, is converted into formic and acetic acids (Dossios, *Jahresb.* 1866, p. 384):



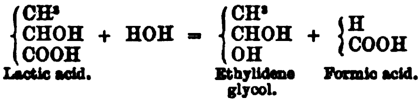
$$\underset{\text{Paralactic.}}{\left\{\begin{matrix}CH^2OH\\CH^2\\COOH\end{matrix}\right.} + O^2 = H^2O + \underset{\text{Malonic.}}{\left\{\begin{matrix}COOH\\CH^2\\COOH\end{matrix}\right.}$$



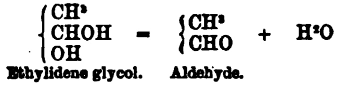
$$\underset{\text{Lactic.}}{\left\{\begin{matrix}CH^3\\CHOH\\COOH\end{matrix}\right.} + O = \underset{\text{Formic.}}{\left\{\begin{matrix}H\\COOH\end{matrix}\right.} + \underset{\text{Acetic.}}{\left\{\begin{matrix}CH^3\\COOH\end{matrix}\right.}$$

According to Chapman and Smith (p. 152), the products are acetic acid, carbon dioxide, and water: $C^3H^6O^3 + O^2 = C^2H^4O^2 + CO^2 + H^2O$.

2. Ordinary lactic acid heated for several hours to 130° with dilute *sulphuric acid* is converted into aldehyde and formic acid:



$$\underset{\text{Lactic acid.}}{\left\{\begin{matrix}CH^3\\CHOH\\COOH\end{matrix}\right.} + HOH = \underset{\text{Ethylidene glycol.}}{\left\{\begin{matrix}CH^3\\CHOH\\OH\end{matrix}\right.} + \underset{\text{Formic acid.}}{\left\{\begin{matrix}H\\COOH\end{matrix}\right.}$$



$$\underset{\text{Ethylidene glycol.}}{\left\{\begin{matrix}CH^3\\CHOH\\OH\end{matrix}\right.} = \underset{\text{Aldehyde.}}{\left\{\begin{matrix}CH^3\\CHO\end{matrix}\right.} + H^2O$$

Paralactic acid similarly treated would probably be resolved into formic acid and ethylene glycol (Erlenmeyer, *Zeitschr. f. Chem.* [2] iv. 343).

3. Lactic acid mixed with *cupric sulphate* forms a deep blue liquid without precipitation, whereas paralactic acid is almost completely precipitated (Dossios, *loc. cit.*).

4. Lactic acid heated to 160°–180° in a stream of gaseous *hydrobromic acid*, or to 100° in sealed tubes with saturated aqueous hydrobromic acid, is converted into bromopropionic acid, $C^3H^5BrO^2$ (Kekulé, *Ann. Ch. Pharm.* cxxx. 11).

5. An ethereal solution of lactic acid treated with *bromine* in a well-cooled vessel, and afterwards heated to 100° in a retort with upright condenser, yields a liquid from which water throws down a gradually crystallising oil, while ordinary lactic acid remains dissolved. The crystalline product, which contains about 6·8 p. c. bromine, is neutral, melts at 83°–85°, dissolves easily in ether, separating therefrom in large acute rhombic prisms, and is decomposed by silver oxide and acetate, also by sodium-amalgam, yielding products not yet examined (Wichelhaus, *Jahresb.* 1867, p. 402).

According to Claus (*Ann. Ch. Pharm.* cxxxvi. 287), calcium lactate yields by dry distillation, acrylic acid, phenol, and a fetid oil varying in boiling point from 75° to 210°. Potassium lactate subjected to electrolysis yields large quantities of carbon dioxide and aldehyde-resin (Brester, *Jahresb.* 1866, p. 87). Ethyl lactate is converted by phosphorus trichloride into ethyl chloropropionate (Frankland a. Duppa. *ibid.* 1865, p. 386):

$$3C^3H^5(C^2H^5)O^3 + PCl^3 = PH^3O^3 + 3C^3H^4Cl(C^2H^5)O^2.$$

Dibromolactic acid, $C^3H^4Br^2O^3$, is formed by enclosing 1 mol. pyroracemic acid, $C^3H^4O^3$ (dried by standing over oil of vitriol and quick lime), with 1 mol. bromine in a sealed tube, and leaving the tube for several hours in ice-cold water. A viscid product containing capillary crystals is then formed, and the colour of the bromine disappears, without perceptible formation of hydrobromic acid. The product quickly absorbs moisture from the air, and decomposes with evolution of hydrobromic acid; it is also decomposed by alcohol, and melts when heated, giving off hydrobromic acid. Its salts have not been prepared. When more than 1 mol. bromine is used, the excess remains free, and may be removed by a stream of dry air. Sodium-amalgam converts the product into ordinary lactic acid. It appears therefore to be dibromolactic acid formed from pyroracemic acid by a simultaneous process of addition and substitution:

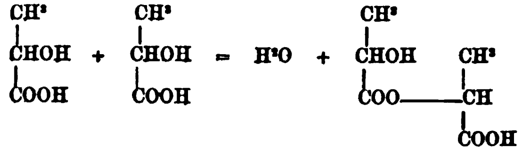
$$\underset{\text{Pyroracemic.}}{\left\{\begin{array}{l}CH^3\\ CO\\ COOH\end{array}\right.} + Br^2 = \left\{\begin{array}{l}CH^2Br\\ CO\\ COOH\end{array}\right. + HBr = \underset{\text{Dibromo-lactic.}}{\left\{\begin{array}{l}CH^2Br\\ CBrOH\\ COOH\end{array}\right.}$$

Dibromolactic acid is converted by water, or by exposure to moist air, into crystalline monobromopyroracemic acid, $C^3H^3BrO^3$. In one experiment, in which considerable quantities of dibromolactic acid were dissolved in water, the crystallised product appeared to have the composition of dibromodilactic acid, $C^6H^8Br^2O^5$ (Wislicenus, *Ann. Ch. Pharm.* cxlviii. 208; *Zeitschr. f. Chem.* [2] v. 255. See also De Clermont a. Silva, *Deut. Chem. Ges. Berlin.* 1869, p. 40).

Benzolactic acid, $C^{10}H^{10}O^4 = \left\{\begin{array}{l}CH^3\\ CHO(C^7H^5O)\\ COOH\end{array}\right.$, which Strecker obtained by heating lactic acid with benzoic acid (i. 561), is also produced by the action of benzoyl chloride on lactates, the calcium salt for example. When recrystallised from water, it always yields, besides the crystallised acid, $C^{10}H^{10}O^4$, an oily hydrate, $C^{10}H^{10}O^4.H^2O$, which in dry air is slowly converted into the crystallised acid. ***Ethyl Benzolactate***, $C^{10}H^9O^4.C^2H^5$, formed by heating ethyl lactate to 100° with benzoyl chloride, or by the action of ethyl iodide on silver benzolactate, is a colourless oily liquid, insoluble in water, miscible in all proportions with alcohol and ether; boiling at 288°; resolved by water at 150° into lactic acid and ethyl benzoate. Alcoholic ammonia converts it into benzolactamide, $C^{10}H^{11}NO^3 = \left\{\begin{array}{l}CH^3\\ CHO(C^7H^5O)\\ CONH^2\end{array}\right.$, which crystallises in white sublimable nodules, melting at 124°, slightly soluble in water, easily in alcohol. By boiling with potash, it is resolved into lactic acid, benzoic acid, and ammonia; alcoholic ammonia converts it into benzamide and lactamide (Wislicenus, *Ann. Ch. Pharm.* cxxxiii. 257; *Jahresb.* 1865, p. 363).

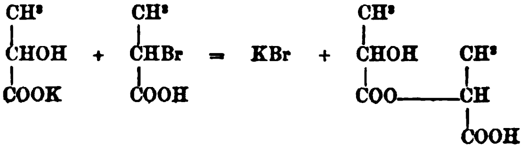
LACTIC ANHYDRIDES. 1. *Lactide.* $C^3H^4O^2$.—According to Krupsky (*Zeitschr. f. Chem.* [2] v. 179), this substance is formed very easily during the distillation of lactic acid, before the temperature rises to 200°, but the most favourable temperature for its production is from 210° to 215°. It may be obtained in splendid rhombic crystals by spontaneous evaporation of its alcoholic solution in a current of air.

2. *Dilactic Acid.* $C^6H^{10}O^5 = \left.\begin{array}{c}(C^3H^4O)''\\ (C^3H^4O)''\\ H^2\end{array}\right\}O^3 = 2C^3H^6O^3 - H^2O$ (iii. 461).—Wislicenus (*Ann. Ch. Pharm.* cxxviii. 1; cxxxiii. 257) regards this compound as an ethereal derivative of two molecules of lactic acid, one of which acts an an acid, the other as an alcohol; thus:



Lactic acid. Lactic acid. Dilactic acid.

This view has recently been corroborated by the experiments of N. von der Bruggen (*Zeitschr. f. Chem.* [2] v. 338), from which it appears that dilactic acid is produced by heating a mixture of equivalent proportions of bromopropionic acid and potassium lactate to 100°-120° in a well-corked flask:



The portion of the product which was soluble in ether gave with dry ammonia the characteristic reaction of dilactic acid, viz. the formation of ammonium lactate and lactamide (p. 769).

A compound isomeric with the neutral ethylic ether of dilactic acid, $C^6H^8(C^2H^5)^2O^5$, is produced by heating ethylic sodio-lactate (iii. 463) with ethylic chloropropionate to 110°–120° for twenty-four hours:

$$C^3H^4NaO^3.C^2H^5 + C^3H^4ClO^2.C^2H^5 = NaCl + C^6H^8O^5.(C^2H^5)^2.$$

The resulting light brown viscid liquid may be freed from sodium chloride by washing with water, and from undecomposed chloropropionic ether by heating it to 110° in a rarefied distillatory apparatus. The distillate is a colourless oil having a faint ethereal odour, not decomposed by aqueous caustic soda even at the boiling heat, but completely, though slowly, by alcoholic soda, yielding lactic and ethyl-lactic acids. By heating it for 24 hours with a large excess of ethereal solution of ammonia, and distilling off the ether and excess of ammonia over the water-bath, there is obtained a non-distillable oil, which, after being left for some time over sulphuric acid in a vacuum, exhibits the composition of ethylic dilactamate, $C^8H^{15}NO^4$. It is not however converted into dilactamide by the further action of ammonia, and when heated with potash yields, not dilactic acid, but a mixture of lactic and ethyl-lactic acids (v. d. Bruggen, *Zeitschr. f. Chem.* [2] v. 250).

Ethylic Succinyl-dilactate, $C^{14}H^{22}O^8 = \left.\begin{matrix}(C^4H^4O^2)''\\(C^3H^4O)^2\\(C^2H^5)^2\end{matrix}\right\}O^4$, is formed by heating 1 mol. succinyl chloride to 100° with rather more than 2 mol. ethyl lactate, and removing the excess of the latter by heating the product to 170° in a stream of air. The compound, purified by solution in alcohol, precipitation by water, and distillation, is a colourless oily liquid, insoluble in water, miscible in all proportions with ether, and boiling between 300° and 304° (Wislicenus, *Ann. Ch. Pharm.* cxxxiii. 257). Wurtz a. Friedel (*Jahresb.* 1861, p. 378) obtained this ether in a less pure state, and with a lower boiling point, by heating neutral potassium succinate with ethylic chlorolactate.

LACTIMIDE, $C^3H^5NO = \left.\begin{matrix}(C^3H^4O)''\\H\end{matrix}\right\}N$, is produced by heating alanine in dry hydrochloric acid gas to 180°–200° as long as water continues to form: $C^3H^7NO^2 - H^2O = C^3H^5NO$. The brown amorphous product, treated with lead hydrate and hydrogen sulphide, and recrystallised from absolute alcohol, yields lactimide in colourless needles, melting at 275°, subliming undecomposed when cautiously heated, having a bitter taste, easily soluble in water and in alcohol. The solution neither dissolves silver oxide, nor gives a precipitate with silver nitrate or zinc chloride. The quantity of lactimide obtained as above is but small, a large portion of the alanine being resolved into carbon dioxide and ethylamine (Preu, *Ann. Ch. Pharm.* cxxxiv. 372).

LACTONIC ACID. Syn. with Isodiglycol-ethylenic Acid (iii 414).

LACTOPROTEIN. See Lactalbumin (p. 769).

LÆVULIN. A substance resembling dextrin, contained in the juice of the tubers of the Jerusalem artichoke, from which it may be separated by repeated treatment with alcohol. It has a sweetish taste; is soluble in water; does not reduce cupric oxide in alkaline solution till it has been boiled with acids; and is optically inactive in its natural state, but becomes strongly lævogyrate by treatment with hydrochloric acid (Ville a. Joulie, *Bull. Soc. Chim.* [2] vii. 262).

LAMPROPHANE. A sulphate, so called on account of its lustre, occurring at Langbanshytta in Wermland, Sweden, in easily cleavable, white, nacreous masses having a sp. gr. = 3·07, and hardness = 3. Analysis gave

SO^3	PbO	MnO	CaO	MgO	K^2O; Na^2O	H^2O	
11·17	28·00	7·90	24·65	5·26	14·02	8·35	= 99·35

(Igelström, *Oefv. af. Kongl. Akad. Förh.* 1866, No. 4, p. 93).

LANGITE. A basic cupric sulphate occurring, together with others, in the clay-slate of Cornwall. (See Sulphates.)

LANTHANUM. Zschiesche (*J. pr. Chem.* civ. 174) has determined the atomic weight of this metal by the decomposition of its sulphate, which at a white heat gives off the whole of its water and sulphuric acid, leaving the pure oxide. Six experiments gave values of La varying from 89·44 to 91·25: mean 90·18.

Cl. Winkler (*J. pr. Chem.* xcv. 410; *Jahresb.* 1865, p. 708) separates lanthanum from didymium in a solution likewise containing cerium, by means of potassium permanganate and mercuric oxide. When a hydrochloric acid solution of the three metals, made as neutral as possible, is mixed with precipitated mercuric oxide, and a dilute solution of potassium permanganate is stirred into it till the colour of the latter disappears, the whole of the lanthanum (together with traces of didymium) remains in solution, whilst the resulting precipitate contains ceric oxide and didymium peroxide, together with mercuric oxide and manganese dioxide. This precipitate, freed from mercuric oxide by ignition, is dissolved in hydrochloric acid; the solution is concentrated by evaporation over sulphuric acid; and the sulphates of cerium and didymium are precipitated by means of solid potassium sulphate. These sulphates, after washing with a concentrated solution of potassium sulphate, are precipitated by ammonium oxalate, and the oxides of cerium and didymium obtained by igniting the precipitated oxalates are separated by known methods. The solution containing the lanthanum, after being freed from mercury by hydrogen sulphide, is precipitated with oxalic acid, and the washed lanthanum oxalate is ignited. The lanthanum oxide thus obtained contains only traces of didymium. This mode of separating lanthanum and didymium succeeds, however, only when cerium is present; in the contrary case only a small quantity of didymium oxide is precipitated.

For the separation of lanthanum and didymium from cerium, see also CERIUM (p. 419).

LANTHOPINE. $C^{23}H^{25}NO^4$ (Hesse, *Ann. Ch. Pharm.* cliii. 57; *Chem. Centr.* 1870, 168).—A base homologous with papaverine, contained in small quantity, together with others, in the aqueous extract of opium. The mode of preparing it given under OPIUM-BASES (*q. v.*) is founded on the fact that lanthopine does not neutralise acetic acid, whereas the other bases present in the aqueous solution form neutral salts therewith: hence lanthopine is precipitated when the acetic solution of the whole of these bases is exactly neutralised with ammonia.

Lanthopine is a white powder consisting of microscopic prisms, or fan-shaped groups of prisms, sometimes a centimetre long; tasteless; does not alter the colour of litmus. Heated to 190°, it turns brown and gradually decomposes. It is insoluble in water, nearly insoluble in alcohol, very slightly soluble in ether and benzol, but dissolves pretty easily in *chloroform*, and separates therefrom on evaporation in small white prisms.

Lanthopine does not neutralise *acids* completely. It is precipitated from the solutions of its salts by *potash-ley* and *milk of lime*, and redissolved by an excess of the reagent; also by *sal-ammoniac*, like morphine and pseudomorphine; but it differs from these bases in not forming a blue solution with ferric chloride. Chloroform extracts it from the lime solution, but not from the potash solution till after addition of sal-ammoniac. Strong *nitric acid* dissolves it with orange-red colour; strong *sulphuric acid* with faint violet colour; acetic acid dissolves it with difficulty.

Sulphate of lanthopine forms extremely thin needles resembling narceine in appearance. The *hydriodide* is a white amorphous precipitate, melting, and ultimately dissolving, in hot water, easily soluble in alcohol. The *hydrochloride*, $C^{23}H^{25}NO^4.HCl + 6H^2O$, forms extremely thin needles resembling narceine, appearing like a jelly in mass, easily soluble in boiling water. The *platinochloride*, $2(C^{23}H^{25}NO^4.HCl).PtCl^4 + 2H^2O$, is a crystalline powder insoluble in water, alcohol, and hydrochloric acid.

LAUDANINE, $C^{20}H^{25}NO^3$ (Hesse, *Ann. Ch. Pharm.* cliii. 527).—A base homologous with morphine and codeine, also contained in the aqueous extract of opium. For its preparation, see OPIUM-BASES.

It crystallises from hot dilute alcohol in stellate groups of small, colourless, six-sided prisms, terminated at both ends by domes. Melts at 165°; solidifies in the crystalline state on cooling; not sublimable. Tasteless. In the crystalline state it dissolves easily in *benzol*, *chloroform*, and boiling *alcohol*; sparingly in cold alcohol, still less in *ether* (1 pt. in 540° at ordinary temperatures); in the amorphous state, that is when recently precipitated, it is much more soluble.

The *salts* of laudanine have a bitter taste. From their solutions *potash* and *ammonia* precipitate the base in white amorphous flocks, which soon become crystalline and dissolve in excess of the precipitant; *chloroform* extracts it from the ammoniacal but not from the potassic solution. Laudanine dissolves in strong *sulphuric acid* with rose-red colour, in strong *nitric acid* with orange-red colour, and in *ferric chloride* with emerald-green colour.

Sulphate of laudanine forms concentric groups of needles very soluble in water. The *hydriodide* forms groups of white crystals, strung together like a necklace, easily soluble in boiling water. The *hydrochloride* crystallises in delicate colourless prisms, easily soluble in water and in alcohol, less soluble in solution of common salt. The *mercurochloride* is a white precipitate, somewhat soluble in boiling water, and separating therefrom in spherical groups of crystals. The *platinochloride*, $2(C^{20}H^{25}NO^4.HCl).PtCl^4 + 2H^2O$, is a yellow amorphous precipitate, easily soluble in water, especially at the boiling heat. *Sulphocyanate of laudanine* forms white crystalline nodules moderately soluble in boiling water.. The *oxalate* crystallises in delicate, concentrically grouped, colourless needles, somewhat sparingly soluble in cold water.

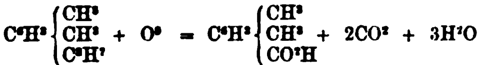
LAURENE or **LAUROL.** $C^{11}H^{16}$.—See BENZENE, HOMOLOGUES OF (p. 304).

LAURIC ACID, $C^{12}H^{24}O^2$, is one of the constituents of the crude oil of bay (Blas, *Ann. Ch. Pharm.* cxxxiv. 1).

LAURITE. A sulphide of ruthenium and osmium, occurring in the platinum ore of Borneo. It forms very small grains or globules, of iron-black colour and strong lustre, and exhibiting faces of the regular octohedron, cube, and other forms of the regular system; very hard and brittle; with perfect octohedral cleavage and flat-conchoïdal fracture; harder than quartz; sp. gr. greater than 6. Decrepitates like galena when heated; does not fuse before the blowpipe, but gives off the odour of sulphurous oxide and afterwards of osmic oxide. It is not attacked even by nitromuriatic acid, or by ignition with acid potassium sulphate, but when fused in a silver crucible with potassium hydrate and nitrate, it dissolves with greenish colour, and the product yields to water a solution containing ruthenium and osmium. The mineral ignited in a stream of hydrogen gives off hydrogen sulphide, but no water. Analysis gave 31·79 p. c. sulphur, 65·18 ruthenium, and 3·03 osmium, agreeing nearly with the formula $OsS^4.12Ru^2S^3$ (Wöhler, *Ann. Ch. Pharm.* cxxxix. 116; *Jahresb.* 1865, p. 913). Laurite is also contained in the platinum ore of Oregon (Wöhler, *Zeitschr. f. Chem.* [2] vi. 85).

LAUROXYLIC ACID. $C^9H^{10}O^2$.—An acid isomeric with xylic or xylylic acid (v. 1062), produced by the action of dilute nitric acid on laurene. It is nearly insoluble in cold, slightly soluble in boiling water, easily in alcohol, and separates from the hot aqueous solution as an indistinct crystalline powder, from alcohol in hard nodules. Melting point 135°. The *barium salt*, $(C^9H^9O^2)^2Ba + 4H^2O$, and the analogously constituted *calcium salt*, are easily soluble in water, and crystallise in concentrically grouped needles; the *silver salt*, $C^9H^9O^2Ag$, is a white precipitate, crystallising in small quantity from hot water.

Lauroxylic acid is further oxidised by chromic acid, the ultimate product being apparently acetic acid. Its constitution and relation to laurene are probably represented by the following equation:



$$C^6H^3\left\{\begin{array}{l}CH^3\\CH^3\\C^3H^7\end{array}\right. + O^6 = C^6H^3\left\{\begin{array}{l}CH^3\\CH^3\\CO^2H\end{array}\right. + 2CO^2 + 3H^2O$$

Laurene. Lauroxylic acid.

(Fittig, Köbrich, a. Jilke, *Ann. Ch. Pharm.* cxlv. 129).

LAWROWITE. A mineral occurring near the river Sljudjanka in Russia, in emerald-green crystals, having the form of pyroxene, with cleavage parallel to the faces of a rhombic prism of 87° 7′. It contains silica, lime, and magnesia, with small quantities of alumina and iron, traces of manganese, and vanadium as colouring matter (Kokscharow, *Jahresb.* 1866, p. 927).

LAZULITE. A summary of the known facts relating to lazulite and ultramarine is given by Schützenberger (*Bull. Soc. ind. de Mulhouse*, mars 1865, p. 97; *abstr. Bull. Soc. Chim.* [2] iii. 455).

LEAD. On the physical properties of pure and impure lead, and on the impurities of commercial lead, see W. Baker (*Practical Mechanic's Journal*, 1864, April 7; *Report 33 of British Assoc., Notices and Abstracts*, p. 32; *Dingl. pol. J.* clxxiii. 119, 122; *Jahresb.* 1864, p. 474).

When granulated lead is boiled with pure water, a slow but continuous evolution of hydrogen takes place (1 to 2 c. c. in ten minutes when 10 to 20 grm. lead are used), the liquid becoming turbid from formation of hydrated lead oxide, and acquiring a strong alkaline reaction. Hydrochloric acid of sp. gr. 1·2 in contact with pure lead gives off hydrogen even at ordinary temperatures, more abundantly when heated, and with the finely divided metal. The evolution of hydrogen from the hydrochloric acid is greatly accelerated, especially at first, by placing metallic copper in contact with the lead. Sulphuric acid of 20 p. c. does not give off hydrogen under the same circumstances (Stolba, *J. pr. Chem.* xciv. 113).

According to Langlois (*J. Pharm.* [4] li. 320), the protection of lead from the action of ordinary water is chiefly due to the presence of calcium bicarbonate. The lead taken up by water which does not contain the carbonates of alkaline earths, such as distilled or rain water, is not dissolved, but suspended, in the form of basic carbonate, and, like the corresponding zinc-compound, may be separated by a thick double paper filter, as effectually as by a charcoal filter. In river water, lead becomes covered with a compact film of suboxide, which protects the metal from further action.

From experiments by Stalman (*Dingl. pol. J.* clxxx. 366; *Jahresb.* 1866, p. 230), it appears that perfectly pure distilled water does not act upon lead, but that the action takes place when the water contains very small quantities of volatile substances (ammonia or nitric acid). The action on the lead requires, moreover, access of air and of free carbonic acid; if the air is completely excluded (as when the lead is placed in a bottle quite full of water), or if the carbonic acid is removed by an absorbing agent, no action takes place. The deposit formed is a mixture of basic carbonates of lead, and the water filtered therefrom is quite free from lead. According to Böttger, also (*Jahresb.* 1866, p. 232), the formation of this deposit is favoured by the presence of a very small quantity of ammonium carbonate in the water, while water perfectly purified by distillation with sulphuric acid has no action on pure lead.

According to Reichelt (*Dingl. pol. J.* clxxii. 155), pure lead immersed in a solution of common salt becomes covered with a crust of hydrate and carbonate of lead, a portion also being dissolved; common commercial salt acts in this manner more quickly than pure sodium chloride. Damp salt in contact with lead or plumbiferous tin also quickly takes up lead.

Estimation.—For the estimation of lead, either in soluble or in insoluble compounds, Stolba (*J. pr. Chem.* ci. 150) heats the compound in a platinum dish with dilute hydrochloric acid and pure zinc till the lead is completely reduced. The spongy lead thus separated is washed on the dish with water containing a drop of sulphuric acid, then dried at 150°–200° and weighed. The oxide thereby produced is dissolved out by cold water containing from 2 to 4 cub. cent. of standard nitric acid, and the quantity of lead thereby dissolved is determined by inverse titration of the remaining nitric acid.

For the *volumetric estimation* of lead, H. Schwarz (*Zeitschr. anal. Chem.* ii. 378, 392; *Jahresb.* 1863, p. 685) precipitates it with a solution of potassium dichromate containing 14·730 grm. of the salt in a litre, each cub. cent. of such a solution corresponding to 0·0207 grm. of lead, and determines the end of the precipitation by mixing a drop of the liquid from which the precipitate has separated with a drop of a solution of silver nitrate on a porcelain plate, whereby a red coloration is produced as soon as the chromate solution is in excess. For this excess a deduction of 1 c. c. is made from the volume of chromate solution used.

The separation of lead from *bismuth* may be effected by means of a solution of ammonio-thallic chloride (v. 748), which precipitates bismuth, but not lead, excepting from the basic acetate (Nicklès, *Bull. Soc. Chim.* [2] v. 49).

Lead may be detected in presence of *silver*, and separated from that metal, by the insolubility of lead chromate in sodium hyposulphite. When a solution containing a little lead and much silver is mixed with excess of sodium hyposulphite, and then with a small quantity of potassium chromate, the whole of the lead is precipitated as chromate (Chancel, *Jahresb.* 1866, p. 803).

The desilvering of lead is facilitated, according to Blagden (*Mechanic's Magazine*, Sept. 1867; *Dingl. pol. J.* clxxxvi. 474), by dissolving about ½ p. c. zinc in the refined metal melted at 540°, and passing a galvanic current through it by means of copper wires for 10 to 30 minutes, or till all the zinc has risen to the surface. This crust of zinc contains the silver, and may be removed after the melted mass has cooled to 450°. For satisfactory desilverisation (to about $\frac{1}{500}$ p. c.) the operation must be repeated several times.

Compounds of Lead.

Chloride. $PbCl^2$.—The solubility of this salt in water and in aqueous hydrochloric acid has been determined by J. C. Bell (*Chem. Soc. J.* [2] xvi. 350; *Chem. News*, xvi. 69): 1 pt. of lead chloride dissolves in 105·2 pts. water at 16·5°, the resulting solution containing 0·9414 p. c. $PbCl^2$. The quantities dissolved by aqueous hydrochloric acid of various strengths are given in the following table:

Quantity of Hydrochloric acid of sp. gr. 1·1162 in 100 pts. of water	Quantity of $PbCl^2$ dissolved at 17·7° by 100 pts. of liquid	Quantity of Hydrochloric acid of sp. gr. 1·1162 in 100 pts. of water	Quantity of $PbCl^2$ dissolved at 17·7° by 100 pts. of liquid
1	0·347	15	0·090
2	0·201	20	0·111
3	0·165	30	0·151
4	0·145	40	0·216
5	0·131	50	0·356
6	0·107	60	0·559
7	0·100	70	0·933
8	0·099	80	1·498
9	0·096	90	2·117
10	0·093	100	2·900

It appears from this table that the dilute acid containing 1·5 p. c. of acid of sp. gr. 1·1162 exhibits a minimum power of dissolving lead chloride at the temperature above specified. For a more extended table see the paper in the *Chemical Society's Journal*.

It is commonly stated that lead chloride crystallises in needles, but according to Bell's observations, the needle-shaped crystals are obtained only from solution in weak hydrochloric acid, whereas from pure water the salt separates in wedge-shaped crystals, and from strong hydrochloric acid in rhombic crystals. The form of the crystals was, however, determined more exactly several years ago by Schabus (*Wien. Akad. Ber.* 1850, April, p. 456), who found that a solution of lead chloride in hydrochloric acid yields by spontaneous evaporation distinct crystals belonging to the rhombic system, and exhibiting the combination $P.2P.oP.\breve{P}\infty.4\breve{P}\infty.\infty P\infty$, and often becoming needle-shaped by predominance of the faces $P.2P.oP$ lying in one zone. Angles $P:P$ in the terminal edges = 134° 24′ and 98° 45′; in the lateral edges = 98° 31′. Cleavage perfect parallel to oP. Sp. gr. = 5·802.

A solution of lead chloride mixed with the chloride of an alkali-metal, and especially with calcium chloride, absorbs a large quantity of chlorine gas, forming a deep yellow solution which may be preserved for a long time in a closed vessel, even if not protected from the solar rays, but in an open vessel is resolved into lead chloride and free chlorine. When added by drops to a large quantity of water, it yields a precipitate of lead dioxide and lead chloride. The dioxide is also precipitated from it by caustic alkalis and alkaline carbonates. With manganous chloride it forms a precipitate of lead chloride and manganese dioxide. It quickly dissolves copper, iron, zinc, gold-leaf, and finely divided platinum, and violently oxidises organic bodies, in all cases with separation of lead chloride, $PbCl^2$. The yellow solution probably contains an unstable tetrachloride of lead, which cannot exist in the separate state. On this supposition the reaction with water may be represented by the equation: $PbCl^4 + 2H^2O = 4HCl + PbO^2$ (Sobrero a. Selmi, *Ann. Ch. Pharm.* lxxvi. 234. Nicklès, *Compt. rend.* lxiii. 1118; *Jahresb.* 1866, p. 232).

Iodide. PbI^2.—This compound in the dry state is not affected by light, and even when moist it undergoes decomposition only in direct sunshine and in contact with the air, iodine being separated, and carbonate and dioxide of lead produced. This decomposition is extremely slow with pure lead iodide, but is accelerated by all substances which absorb iodine. Lead chloride is not altered by light (W. Schmid, *Pogg. Ann.* cxxvii. 493).

Oxide. PbO.—The hydrate, $3PbO.H^2O$, may be obtained in strongly refracting octohedral crystals, by mixing 100 vol. of an aqueous solution of the basic acetate, $3PbO.C^4H^6O^4 + H^2O$ or $2PbO.C^4H^6PbO^4 + H^2O$ (p. 11), with 50 vol. of deaërated water, and then with a mixture of 20 vol. ammonia and 30 vol. water, and leaving the solution exposed to a temperature of 25°–30°. When a mixture of 100 vol. of the solution of the triplumbic acetate saturated at 15° to 16°, and 50 vol. water boiled for a short time and then left to stand in boiling water, is mixed with 3 vol. ammonia and 20 vol. water previously heated to 80°, anhydrous lead oxide is deposited in the course of a minute, in yellowish rhomboïdal lamellæ which unite in radiate groups (Payen, *Ann. Ch. Phys.* [4] viii. 302).

An alkaline solution of lead oxide is precipitated by alkaline solutions of *chromic, stannic, stannous, antimonious*, and *arsenious oxides*. The precipitate formed under these circumstances by arsenious oxide is the triplumbic arsenite $Pb^3As^2O^6$ (Streng, *Ann. Ch. Pharm.* cxxix. 238).

Sulphide. PbS.—Hydrogen sulphide passed into lead solutions sufficiently acidulated with nitric acid, immediately forms a heavy pulverulent precipitate formed of microscopic cubes resembling galena. A solution of 3 grms. lead nitrate in 250 c. c. 10 p. c. nitric acid, gave at 15° cubes measuring 0·19 mm.; at 40°–90° cubes of 0·025 to 0·028 mm. in the side. Solutions prepared in the same proportions, but with nitric acid of 1 p. c., yielded first a granular or amorphous precipitate; afterwards, when the quantity of free acid had increased in proportion to the lead salt, a crystalline precipitate. Lead solutions strongly acidulated with acetic acid give, on the other hand, with hydrogen sulphide, an amorphous precipitate. The iridescent film which is formed in the precipitation of neutral or slightly acid solutions by hydrogen sulphide, and dries up to shining spangles, is likewise non-crystalline. Roll-sulphur left for some time in a solution of lead oxide in caustic potash, produces, together with amorphous lead sulphide, cubes of this compound large enough to be distinguished by the naked eye (F. Muck, *Zeitschr. f. Chem.* [2] iv. 241).

LECANORIC ACID. $C^{16}H^{14}O^7$.—Hesse (*Ann. Ch. Pharm.* cxxxix. 22) prepares this acid from *Roccella fuciformis* or *R. tinctoria* by exhausting the lichen with ether, dissolving the greenish-white crystalline residue left on evaporation in milk of lime, precipitating the filtrate with sulphuric acid, washing the precipitate with water, and recrystallising it from hot alcohol. The exhaustion of the lichen in the first instance by milk of lime, Hesse finds less advantageous, because the acid separated from the gelatinous solution is contaminated with a yellow-brown colouring matter which can only be removed by repeated crystallisation from alcohol. In either case the purified acid must be treated with a quantity of ether less than sufficient to dissolve it, whereby a difficultly soluble substance is removed. The ethereal solution is then evaporated, and the residue again crystallised from hot alcohol.

The acid thus prepared has the composition $C^{16}H^{14}O^7 . H^2O$ assigned to it by Schunck, and easily gives off its water (5·35 p. c.) at 100°. 1 pt. of the acid dissolves in 24 pts. ether at 20° (according to Schunck in 80 pts. at 15°); it melts at 153° to a colourless liquid which quickly decomposes, with evolution of carbon dioxide. By passing this gas through a solution of the acid in baryta-water, a very stable solution of barium lecanorate is obtained; this reaction affords a means of separating lecanoric acid from erythrin. When the solution of this barium salt is boiled with excess of baryta till it no longer yields a gelatinous precipitate with hydrochloric acid, it deposits on cooling crystals of orsellinic acid. By boiling lecanoric acid with alcohol, ethyl orsellinate is produced:

$$\underset{\substack{\text{Lecanoric}\\\text{acid}}}{C^{16}H^{14}O^7} + C^2H^6O = CO^2 + \underset{\text{Orcin}}{C^7H^8O^2} + \underset{\substack{\text{Ethyl}\\\text{orsellinate}}}{C^8H^7(C^2H^5)O^4};$$

but the quantity of this ether obtained is always less than the theoretical amount (57·6 instead of 61·6 p. c.), because part of the lecanoric acid is decomposed by the water in the alcohol, in the manner shown by the equation:

$$\underset{\substack{\text{Lecanoric}\\\text{acid.}}}{C^{16}H^{14}O^7} + H^2O = CO^2 + \underset{\text{Orcin.}}{C^7H^8O^2} + \underset{\substack{\text{Orsellinic}\\\text{acid.}}}{C^8H^8O^4}$$

With amylic alcohol in like manner amyl orsellinate is produced.

Grimaux (*Bull. Soc. Chim.* [2] iii. 410), regarding orsellinic acid as a monobasic but triatomic acid, $\left.\begin{matrix}(C^8H^4O)'''\\H^3\end{matrix}\right\}O^3$ (inasmuch as it is converted by abstraction of CO^2 into the diatomic compound, orcin, $C^7H^6(OH)^2$), represents lecanoric acid by the formula $\left.\begin{matrix}(C^8H^5O)'''\\(C^8H^4O)'''\\H^4\end{matrix}\right\}O^5$.

Dibromolecanoric acid, $C^{16}H^{12}Br^2O^7$, is produced by mixing the ethereal solution of lecanoric acid by small portions with an ethereal solution of bromine, till the latter is but slowly absorbed. By washing the evaporation-residue with water, and recrystallising from hot alcohol with addition of animal charcoal, it is obtained in white crystals insoluble in water, less soluble in alcohol and ether than lecanoric acid, and producing in alcoholic solution a purple-violet colour with ferric chloride, blood-red with chloride of lime. It melts at 175°, with evolution of carbon dioxide, and is decomposed by boiling with baryta-water, yielding barium bromide and carbonate, and a yellow substance (Hesse).

Tetrabromolecanoric acid, $C^{16}H^{10}Br^4O^7$, is formed by dropping bromine into an ethereal solution of lecanoric acid, and crystallises from alcohol in pale yellow prisms melting at about 157°, easily soluble in alcohol, ether, ammonia, and baryta-water, and precipitated from the latter by acids in the form of a yellowish oil. Its alcoholic solution has an acid reaction, and reacts with ferric chloride and chloride of lime like that of the dibrominated acid. Boiled with baryta-water it yields barium bromide and carbonate, together with a yellow resinous substance (Hesse).

LECITHINE (Diakonow, *Centralb. f. die med. Wissensch.* 1867, No. 1 and 7; *Med.-chem. Unters.* ii. 221; *Zeitschr. f. Chem.* [2] iv. 154. Strecker, *Zeitschr. f. Chem.* [2] iv. 437).—This name was applied by Gobley to a phosphoretted fatty body which he supposed to exist in the yolk of eggs, the brain, bile, blood, &c., but did not succeed in isolating (iii. 567). Phosphoretted fats, existing in the brain and other parts of the animal organism, have also been described as *oleophosphoric acid* and *protagon*. These phosphoretted compounds were shown by Gobley to yield by saponification fatty acids and glycerophosphoric acid, and Liebreich obtained from his protagon a strong base, called neurine or choline (p. 448). More recently, Diakonow has obtained from the yolk of hens' eggs, and from the eggs of the sturgeon, a definite phosphoretted fat, having the composition $C^{44}H^{90}NPO^9 + H^2O$, and resolved by boiling with baryta-water into stearic acid, glycerophosphoric acid, and neurine. This substance, designated especially as lecithine, is regarded by Diakonow as a saline compound of neurine. In accordance with this view, Strecker finds that the ethereo-alcoholic extract of egg-yolk gives with an alcoholic solution of platinic chloride containing free hydrochloric acid, a yellow flocculent precipitate consisting of a compound of platinic chloride with lecithine. This precipitate decomposed by hydrogen sulphide yields a hydrochloride of lecithine; and on agitating the alcoholic solution of this salt with silver oxide, and treating the filtrate with hydrogen sulphide to remove dissolved silver, lecithine is obtained in the form of a waxy substance. The ethereo-alcoholic extract of egg-yolk also yields with cadmium chloride a precipitate of a double salt, from which lecithine may be obtained.

Lecithine thus prepared, when boiled with baryta-water, yields choline, together with glycerophosphoric, oleic, and palmitic acids, and probably small quantities of stearic acid. It appears, therefore, to contain, not merely a single fatty acid, but, like most animal fats, oleic acid, together with solid fatty acids, among which palmitic acid is the most abundant. There are probably, therefore, many varieties of lecithine and numerous mixtures of those varieties.

Strecker represents the lecithines by the general formula:

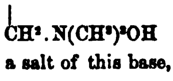
$$\left.\begin{array}{r}2C^nH^{2n}O^2\\ \text{or } 2C^nH^{2n-2}O^2\end{array}\right\} + C^3H^9PO^6 + C^5H^{15}NO^2 - 3H^2O.$$

$$\underset{\text{Fatty acids or Oleic acids.}}{} \qquad \underset{\text{Glycerophosphoric acid.}}{} \qquad \underset{\text{Choline.}}{}$$

The particular lecithine examined by Strecker agreed nearly with the formula $C^{42}H^{84}NPO^9$, obtained by substituting, in the first term of the preceding formula, 1 mol. palmitic acid and 1 mol. oleic acid, whereby it becomes $\left.\begin{array}{l}C^{16}H^{32}O^2\\ C^{18}H^{34}O^2\end{array}\right\}$. This formula agrees also nearly with Diakonow's analysis of lecithine:

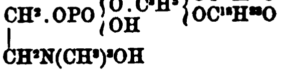
	Calc.	Strecker	Diakonow
C^{42} . .	64·8	64·6	64·3
H^{84} . .	10·6	10·7	11·4
N . .	3·9	4·0	3·8
P . .	1·8	—	1·8

Choline, which, as shown by Wurtz, may be obtained from ethylene oxide and trimethylamine hydrochloride (p. 448), may be regarded as an alcoholic base and represented by the formula



$$\begin{array}{l}CH^2.OH\\ |\\ CH^2.N(CH^3)^3OH\end{array}$$

and lecithine may be regarded as a salt of this base, represented by the formula



$$\begin{array}{l}CH^2.OPO\left\{\begin{array}{l}O.C^3H^5\left\{\begin{array}{l}OC^{16}H^{31}O\\ OC^{18}H^{33}O\end{array}\right.\\ OH\end{array}\right.\\ |\\ CH^2N(CH^3)^3OH\end{array}$$

containing the residues of palmitic acid, oleic acid, and glycerophosphoric acid:

$$PO\left\{\begin{array}{l}OH\\ OH\\ O.C^3H^5(OH)^2.\end{array}\right.$$

Strecker has further pointed out that Liebreich's protagon, which also yields choline by decomposition with alkalis, has the composition of a mixture of lecithine with a non-phosphoretted substance, probably cerebrin:

Lecithine (Diakonow)	Protagon (Liebreich)	Cerebrin (Müller)
64·37	66·2 to 67·4	68·45
11·40	11·1 „ 11·9	11·27
1·80	2·7 „ 2·9	4·61
3·80	1·1 „ 1·5	—
18·73	—	15·67
100·00		100·00

LECYTHIS. See SAPUCAIA (v. 195).

LEGUMIN. The composition of this proteide has recently been examined by Ritthausen (*Zeitschr. f. Chem.* [2] iv. 541). It was prepared by macerating the pulverised seeds of peas, beans, lentils, and vetches, with cold water (in some cases with addition of a little alkali); precipitating the strained liquid with acetic acid; washing the precipitate on a filter with alcohol of 49 to 50 p. c., which caused it to shrink and separate easily from the filter; again exhausting the separated lumps with alcohol, then with ether; removing the liquid as completely as possible by pressure; and finally drying the mass in a vacuum over sulphuric acid The purity of legumin may be known by the three following characters taken together: 1. It dissolves completely in water.—2. Boiled for a few minutes with sulphuric acid diluted with an equal bulk of water, it forms a clear brown-yellow solution, which remains clear on addition of more water.—3. On dissolving it in water containing potash, adding a few drops of solution of cupric sulphate and then a few drops of potash-ley, a violet or reddish-violet colour is produced. Legumin which does not fulfil all these conditions may be purified by solution in weak aqueous potash (containing 1 to 2 p. c. KHO) and reprecipitation.

Legumin, free from ash, obtained from peas, lentils, vetches, and field-beans, gave by analysis in 100 pts.:

C	H	N	O	S
51·48	7·02	16·77	24·33	0·40;

that from garden-beans gave

C	H	N	O	S
51·48	6·92	14·71	26·35	0·45.

The phosphorus in legumin appears to be in the form of phosphoric acid. The possibility of extracting legumin from the seeds by water appears to depend on the presence of mineral substances, especially of tripotassic phosphate and free potash, both of which in aqueous solution easily dissolve pure legumin. Wheat-flour and soft peas do not contain basic phosphates, and from these the protein-substance cannot be dissolved out by water.

Legumin treated with sulphuric acid yields tyrosine, leucine, glutamic acid (p. 636), active aspartic acid (formerly regarded by Ritthausen as a peculiar acid, and called *legamic acid*), and brown amorphous substances.

Substances very closely allied to the legumin of peas, beans, &c., but exhibiting slight diversities in composition and physical properties, are obtained from almonds, the kernels of plums, apricots, and hazel-nuts, white mustard, the seeds of lupines, and oats. The legumin of almonds and lupines (Ritthausen's *conglutin*) is richer in nitrogen (16·65 to 18·93 p. c.) than that of pulse; it is also more glutinous and more soluble in acetic acid (Ritthausen, *J. pr. Chem.* ciii. 65, 78, 193, 273; *Zeitschr. f. Chem.* [2] iv. 528, 541; vi. 126; *Gmelin's Handbook*, xviii. 427–437).

LEPIDENE. $C^{28}H^{20}O$ (Zinin, *Ann. Ch. Phys.* [4] xii. 111; *Jahresb.* 1867, p. 416. Limpricht, *Zeitschr. f. Chem.* [2] v. 336. Dorn, *ibid.* 597).—This compound is formed, together with dibenzyl and an oily body, when benzoïn ($C^{14}H^{12}O^2$) is heated for several hours to 130° with 1½ pt. of fuming hydrochloric acid saturated at + 8°, whereby the benzoïn is converted into an oily body which floats on the surface, and on opening the tube immediately solidifies to a yellow laminar mass. More dilute acid acts only at 170°. The laminar mass is resolved by treatment with solvents into lepidene (28 p. c.), sparingly soluble in alcohol and ether, and partly remaining undissolved when the product is treated with ether, partly crystallising in white scales when the ethereal solution is mixed with alcohol and the ether is distilled off; benzyl (about 40 p. c.), which crystallises from the yellow solution; and a thick oil insoluble in water, but easily soluble in alcohol and ether.

Lepidene is insoluble in water, soluble in 170 pts. of boiling, scarcely soluble in

1,000 pts. of cold alcohol of 94 p. c.; soluble in 38 pts. of boiling and about 52 pts. of cold ether; in 28 pts. boiling and about 500 pts. cold glacial acetic acid; in 2 pts. hot and 1 pt. cold benzol. From solution in alcohol or acetic acid, it crystallises in feathery or laminated groups of flat needles; melts somewhat above 175° to a colourless liquid; and solidifies again in the crystalline form only when the temperature has not been raised above a certain point. At 220° it boils and may be distilled undecomposed in quantities not exceeding 10 grams. It is not decomposed by alcoholic potash-solution or even by fusion with potassium hydrate. Nitric acid of sp. gr. 1·3 converts it into oxylepidene. When gently heated with phosphorus pentachloride, it forms a reddish liquid, which solidifies when washed with water, dissolves easily in alcohol and ether, and crystallises therefrom in needles (Zinin).

Dibromolepidene, $C^{28}H^{18}Br^2O$, is formed on adding bromine in slight excess to a solution of lepidene in acetic acid, and separates in needle-shaped crystals insoluble in water, soluble in 410 pts. of hot alcohol, 66 pts. of boiling acetic acid, and 50 pts. of boiling ether, and crystallises therefrom in thin tables or laminæ. It melts at 190°, and solidifies in the crystalline or amorphous state, according to the temperature to which it has been raised. With nitric acid it forms a needle-shaped body which reacts similarly to oxylepidene.

Oxylepidene, $C^{28}H^{20}O^2$, is most readily prepared by heating lepidene to the boiling point with 10 pts. of glacial acetic acid, and adding a mixture of 1 pt. nitric acid of sp. gr. 1·5 and 3 pts. glacial acetic acid, the oxylepidene then crystallising out on cooling. It forms yellow needles (4-sided prisms) insoluble in water, nearly insoluble in ether and cold alcohol, soluble in 200 pts. of boiling alcohol of 94 p. c., in 22 pts. of hot acetic acid, and easily in benzene. It melts at 220° and resolidifies in the crystalline form on cooling; but after being heated to its boiling point, it forms on cooling a yellow resinous substance, easily soluble in alcohol and ether, and separating therefrom with different properties. Oxylepidene dissolved in hot acetic acid is completely reduced by zinc to lepidene; by boiling with alcoholic potash-solution it is converted into a crystalline body, separable by water and differing in its properties from oxylepidene (Zinin).

Lepidene and oxylepidene are analogous in composition to thionessal and tolallyl sulphide; thus:

Lepidene,	$C^{28}H^{20}O$	Oxylepidene,	$C^{28}H^{20}O^2$
Thionessal,	$C^{28}H^{20}S$	Tolallyl sulphide,	$C^{28}H^{20}S^2$,

and may be formed from thionessal and tolallyl sulphide respectively by treatment with hydrochloric acid and potassium chlorate (Limpricht).

Oxylepidene is converted by the most various reducing agents into lepidene, but the latter cannot be deprived of any further portion of oxygen, even by passing it over heated zinc-powder. Oxylepidene heated with phosphorus pentachloride yields the same products as lepidene, namely, chlorinated derivatives of the latter. The following compounds have been obtained by Dorn:

Dichloroxylepidene, $C^{28}H^{18}Cl^2O^2$, is prepared by treating dichlorothionessal with hydrochloric acid and potassium chlorate. It forms white needles melting at 178°, and is converted by reducing agents into dichlorolepidene, $C^{28}H^{18}Cl^2O$, which forms white needles melting at 156°.

Oxylepidene heated in sealed tubes with phosphorus pentachloride, or (to diminish the pressure) with phosphorus oxychloride, yielded:

1. *Pentachlorolepidene*, $C^{28}H^{15}Cl^5O$, in white crystals melting at 186°, very slightly soluble in alcohol and ether.—2. *Hexchlorolepidene*, $C^{28}H^{14}Cl^6O$, a yellow amorphous substance, melting at 80°–90°, easily soluble in alcohol and ether.—3. *Octochlorolepidene*, $C^{28}H^{12}Cl^8O$, an orange-yellow amorphous substance, softening at 70°, melting at 97°, easily soluble in alcohol and ether.

LEPIDOMELANE. This variety of mica, hitherto found only at one locality in Sweden (iii. 574), occurs, together with danalite, another variety of mica called *cryophyllite*, and a zircon-like mineral, in the granite of Rockport, Massachusetts. The lepidomelane occurs in black six-sided prisms with dark green streak, hardness about 3, and sp. gr. 3·169. Analysis gave:

SiO^2	SiF^4	Al^2O^3	Mn^2O^3	Fe^2O^3	FeO	MgO	K^2O	Li^2O	H^2O	
39·55	0·62	16·73	0·60	12·07	17·48	0·62	10·66	0·59	1·50	= 100·42,

agreeing with the general formula $(M^4; M^3)SiO^4$ (J. P. Cooke, jun., *Sill. Am. J.* [2] xliii. 217).

LEUCANILINE. On the methylated derivatives of this base, produced by the decomposition of iodine-green, see ANILINE (p. 764).

LEUCHTENBERGITE. According to an analysis of this mineral from the Chichime mountains in the Ural, by Duke Nicolas von Leuchtenberg (*N. Petersb. Acad. Bull.* ix. 188; *Jahresb.* 1865, p. 891), it appears to be a distinct mineral species allied to the chlorites.

LEUCIC ACID. $C^6H^{12}O^3 = \begin{array}{l} C^5H^{10}OH \\ | \\ COOH \end{array}$.—Geuther (*Jahresb.* 1867, p. 454) has pointed out the following differences between the salts of this acid and those of its isomeride, diethoxalic acid (iv. 273). The *ammonium salt* of diethoxalic acid crystallises by spontaneous evaporation over sulphuric acid in large laminæ; ammonium leucate is amorphous. *Zinc diethoxalate* forms wavellitic groups of needles, anhydrous, less soluble in alcohol than in water; zinc leucate crystallises in scales containing 1 mol. water, more soluble in hot alcohol than in water. *Cupric diethoxalate* is easily soluble and uncrystallisable; the leucate is a sparingly soluble precipitate. *Silver diethoxalate* contains 1 mol. water; silver leucate is anhydrous.

LEUCINE or **AMIDOCAPROIC ACID.** $C^6H^{13}NO^2 = \begin{array}{l} C^5H^{10}(NH^2) \\ | \\ COOH \end{array}$.—This compound heated in a sealed tube with fuming hydriodic acid is decomposed, with formation of caproic acid and ammonium iodide, and separation of iodine:

$$C^6H^{13}NO^2 + 3HI = C^6H^{12}O^2 + NH^4I + I^2.$$

Conversely it is produced synthetically by heating bromocaproic acid with strong aqueous ammonia to 120°–130° for five or six hours in a sealed tube:

$$C^6H^{11}BrO^2 + NH^3 = HBr + C^6H^{13}NO^2$$

(Hüfner, *Zeitschr. f. Chem.* [2] iv. 391, 616).

In the preparation of leucine by the action of hydrochloric and hydrocyanic acids on valeral-ammonia (iii. 581), the crystalline hydrochloride of the base $C^{18}H^{33}N^5$, discovered by H. Strecker (*Jahresb.* 1864, p. 417), is first produced, and this base, by prolonged contact with hydrochloric acid, is resolved into ammonia and leucine:

$$3C^5H^{10}O + 2NH^3 + 3CNH = 3H^2O + C^{18}H^{33}N^5$$

and

$$C^{18}H^{33}N^5 + 6H^2O = 2NH^3 + 3C^6H^{13}NO^2.$$

After the excess of hydrochloric acid has been removed by evaporation, the greater part of the leucine may be precipitated by ammonia; the portion remaining in solution may be recovered by evaporating, redissolving in hydrochloric acid, and again precipitating with ammonia. The removal of the sal-ammoniac by lead-hydrate, as in Limpricht's process (iii. 580), is not to be recommended, because leucine forms a sparingly soluble compound with lead oxide. Leucine solutions boiled with cupric acetate form a blue crystalline precipitate of *copper-leucine*.

Leucine melts at 210°, and when heated to 220°–230° is converted, with loss of weight amounting to about 20 p. c., into leucimide, $C^6H^{11}NO = (C^6H^{10}O)''NH$, which after repeated crystallisation from alcohol, forms slender needles, subliming in white flocks without previous fusion. Sal-ammoniac and a small quantity of amylamine are formed at the same time as secondary products (Köhler, *Ann. Ch. Pharm.* cxxxiv. 36).

LEUCOPYRITE. This name is given by Zepharovich (*Jahresb.* 1867, p. 973) to an arsenide of iron, Fe^4As^6, occurring, together with löllingite, (Fe^4As^3), in the siderite vein at Hüttenberg in Carinthia. It is found also in a sparry siderite in the Schwarzgrubner vein at Przibram.

LEUCOROSOLIC ACID. See Rosolic Acid.

LEVULIN. See Lævulin.

LIGHT. *Relations between Refractive Power and Chemical Composition.*—The researches of Gladstone and Dale, of which an account is given in the article Light (iii. 624–631), showed: 1. That the specific refractive energy of a liquid—expressed by the formula $\frac{\mu - 1}{d}$, in which μ is the index of refraction, and d the density—is nearly a constant quantity unaffected by change of temperature.—2. That the specific refractive energy of a mixed liquid is approximately the mean of the specific refractive energies of its constituents.—3. That isomeric bodies exhibit in many instances equal specific refractive energies.—4. That in compounds belonging to the same homologous series, the specific refractive energy increases as the series advances, but that the amount of its variation is less between the higher than between the lower terms of the series.

Landolt (*Pogg. Ann.* cxxii. 545; cxxiii. 595; *Jahresb.* 1864, p. 101) simplifies the expression of these relations, especially of the last, by adopting, instead of the specific refractive energy, the product of this fraction by the molecular weight of the compound, $P.\frac{\mu-1}{d}$; this is called the refraction-equivalent. In homologous series the refraction increases in all cases for a difference of CH^2, by a nearly equal amount, the mean increment in the fatty acids, alcohols, &c., being 7·60. The first and third of the above laws remain true for refraction-equivalents to the same extent as for specific refractive energies. The expression of the second becomes: *The refraction-equivalent of a mixture or compound is the sum of the refraction-equivalents of its components.*

This last law gives the means of determining the refraction-equivalents of elements from those of their compounds. Landolt has shown, by comparison of the optical properties of a large number of organic compounds, that the refraction-equivalent is increased by addition of either carbon, hydrogen, or oxygen, but by somewhat different amounts according to the type to which the compound belongs, these values varying for C from 4·75 to 5·43, for H from 1·06 to 1·33, for O from 2·45 to 3·24. The mean refraction-equivalents of these three elements in the homologous fatty alcohols and acids are:

C	H	O[*]
5·00	1·30	3·00

By means of these values, the refraction-equivalent R of a compound of carbon, hydrogen, and oxygen may be calculated according to the formula,

$$R = mr + m'r' + m''r'',$$

where m, m', m'' denote the numbers of the atoms of the three elements, and r, r', r'' their refraction-equivalent: thus in the case of ethyl oxide, $C^4H^{10}O$:

$$4 \times 5·0 + 10 \times 1·3 + 3·0 = 36·0$$

Refraction-equivalent deduced from observation . . . = 36·26.

The values above given for the refraction-equivalents of C, H, and O agree very nearly with those deduced from the experiments of Gladstone and Dale already cited. Gladstone has subsequently determined, by similar methods, the refraction-equivalents of chlorine, bromine, tin, iodine, and mercury; and Haagen (*Pogg. Ann.* cxxxi. 117), by examining a variety of liquid haloïd compounds, has deduced for several of these elements, refraction-equivalents agreeing with those found by Gladstone, together with those of arsenic, antimony, and silicon.

The fact, previously established by Gladstone and Dale, that a substance when dissolved retains the same specific refractive energy, and consequently the same refraction-equivalent, as in the solid state, affords the means of determining the refraction-equivalents of a great number of solid bodies which could not otherwise be ascertained. By determining the refractive indices of a series of chlorides, bromides, and iodides dissolved in water, Gladstone has shown that a chloride has, in each case, a refraction-equivalent about 6 less than the corresponding bromide, and about 17 less than the corresponding iodide; and that a potassium salt has, in each case, a refraction-equivalent about 3·2 greater than that of the corresponding sodium salt, about 4 greater than the lithium salt, and about 3·5 less than the ammonium salt. Hence it seems to follow: 1. That the different salts are really comparable with one another in this respect.—2. That each halogen and each metal retains its own refractive power, with whatever other elements it is combined.—3. That if the value of any one of these elements can be ascertained with certainty, all the rest may also be determined.

Experiments conducted on these principles have been extended by Gladstone to about 180 different salts, containing 28 inorganic salt-radicles and 33 metals. The results are tabulated in a paper recently communicated to the Royal Society (*Phil. Trans.* 1870, p. 9; abstr. *Proc. Roy. Soc.* 1868, p. 439).

The refraction-equivalents of the elementary bodies deduced from these results are given in the following table:

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[*] These values differ but slightly from those of the free elements deduced by Landolt from the observations of Schrarf, Dulong, and Regnault, viz. C = 4·85, H = 1·54, O = 3·04.

Refraction-equivalents of the Elementary Bodies.

Element	Atomic weight	Refraction-equivalent
Aluminium	27·4	8·4
Antimony	122	24·5
Arsenic	75	15·4 (other values ?)
Barium	137	15·8
Bismuth	210	39·2
Boron	11	4·0
Bromine	80	15·3 In dissolved salts 16·9
Cadmium	112	13·6
Cæsium	133	13·7 ?
Calcium	40	10·4
Carbon	12	5·0
Cerium	92	13·6 ?
Chlorine	35·5	9·9 In dissolved salts 10·7
Chromium	52·2	15·9 In chromates 23 ?
Cobalt	58·8	10·8
Copper	63·4	11·6
Didymium	96	16·0 ?
Fluorine	19	1·4 ?
Glucinum	9·4	5·7
Gold	197	24·0
Hydrogen	1	1·3 In hydracids 3·5
Iodine	127	24·5 In dissolved salts 27·2
Iron	56	12·0 In ferric salts 20·1
Lead	207	24·8
Lithium	7	3·8
Magnesium	24	7·0
Manganese	55	12·2 In permanganate 26·2 ?
Mercury	200	21·3 In compound iodides 29·0
Nickel	58·8	10·4
Nitrogen	14	4·1 In high oxides 5·3
Oxygen	16	2·9
Palladium	106·5	22·2
Phosphorus	31	18·3 (other values ?)
Platinum	197·4	26·0
Potassium	39·1	8·1
Rhodium	104·4	24·2 ?
Rubidium	85·4	14·0
Silicon	28	7·5 ? In silicates 6·8
Silver	108	13·5 (other values ?)
Sodium	23	4·8
Strontium	87·5	13·6
Sulphur	32	16·0 (other values ?)
Thallium	204	21·6 ?
Tin	118	27·0 In tetrachloride 19·2
Titanium	50	25·5 ?
Uranium	120	10·8
Vanadium	51·2	25·3 ?
Zinc	65·2	10·2
Zirconium	89·6	22·3 ?

The sign ? in the above table indicates that the equivalent has been deduced from only one compound, or that the different determinations are not fairly accordant.

It will be seen that many of these elements have a double value. An element usually exerts the same influence on transmitted rays in all analogous compounds, and in many that are not analogous; but there are differences of composition which do affect this quality, and in some cases at least these are coincident with a change of atomicity. Thus iron in all the ferrous salts examined has the equivalent 12·0, but in the ferric salts 20·1. The knowledge of this can be applied to the examination of other compounds of the same element, such as the ferricyanide of potassium. The refraction-equivalent of this body gives for iron 11·7, suggesting that the metal is in the same condition as in the ferrous salts.

Again, in most of the vegetable acids, as in other organic compounds, hydrogen has a refraction-equivalent of 1·3, but in hydrochloric, hydrobromic, and hydriodic acids it exerts a far greater influence on light, its refraction-equivalent in these compounds being 3·5.

The bodies of the aromatic group, two series of nitrogenised bases, viz. the pyridine series and chinoline series, and certain oxidised essential oils, exhibit refraction-equivalents considerably higher than those calculated from the values of the elements in the preceding table; for example:

Substance	Formula	Refraction-equivalent		Difference
		Observed	Calculated	
Benzene	C^6H^6	43·7	37·8	5·9
Aniline	C^6H^7N	51·1	43·2	7·9
Salicylol	C^7H^6O	58·9	48·6	10·3
Pyridine	C^5H^5N	40·1	35·6	4·5
Chinoline	C^9H^7N	66·7	58·2	8·5
Naphthalene	$C^{10}H^8$	75·0	60·4	14·6
Anethol	$C^{10}H^{12}O$	81·4	68·5	12·9
Eugenol	$C^{10}H^{12}O^2$	81·1	71·4	9·7
Anthracene	$C^{14}H^{10}$	100·3	83·0	17·3

(Gladstone, *Chem. Soc. J.* [2] viii. 147).

The specific refractive energies, $\frac{\mu-1}{d}$, of the metals are for the most part greater as their combining proportions are less. This will be seen from the following numbers extracted from Gladstone's table (*ibid.* p. 113):

	H	Li	Mg	Fe	Pd	Pt	Pb	Th
Combining proportion	1	4·7	12	28	26·6	49·3	103·5	204
Sp. refr. energy $\frac{\mu-1}{d}$.	1300	540	292	214	208	132	120	103

There are, however, many exceptions to this rule.

On the application of specific refractive energies to the quantitative analysis of mixtures of organic liquids, such as methyl and ethyl alcohol, which cannot be accurately separated by chemical methods, see Landolt (*Ann. Ch. Pharm. Suppl.* iv. 1; *Zeitschr. anal. Chem.* iv. 390; *Jahresb.* 1865, p. 680).

On the relations between refracting power and chemical composition, see also Schrauf (*Pogg. Ann.* cxviii. 359; cxix. 461, 553; cxxvi. 177; cxxvii. 175, 344; *Jahresb.* 1863, p. 98; 1865, p. 84); J. Regnault (*J. Pharm.* [3] xliii. 187; xliv. 187); Fouqué (*Compt. rend.* lxiv. 121; *Phil. Mag.* [4] xxxiii. 555; *Jahresb.* 1867, p. 96).

Fluorescence.—When, instead of observing fluorescence directly, a pure linear spectrum of the fluorescent light is subjected to prismatic analysis, it is found that, for each fluorescent substance, the fluorescence begins at a distinct prismatic colour, and is not excited by any rays of lower refrangibility. When sunlight is used, both the limit of the fluorescence and its maximum intensity, for each particular substance, are situated (with slight variations) at the same part of the spectrum, and are therefore characteristic of that substance. Throughout the whole extent of the fluorescent portion of the spectrum, the predominant tints in the secondary spectrum are the same, so that the composition of the fluorescent colour is independent of the nature of the colour which excites it, and is likewise characteristic of each fluorescent substance. In light from artificial sources, or light which has passed through coloured media, the beginning and maximum of the fluorescence may be situated at points of the spectrum different from those at which they are placed in sunlight.

Composite fluorescences, such as those of tincture of litmus and alcoholic tincture of quassia, exhibit, by prismatic analysis of the linear spectrum, several secondary spectra. Mixtures of fluorescent substances, on the other hand, exhibit either a composite fluorescence (which may be resolved by prismatic analysis into simple fluorescences), or a fluorescence which cannot be recognised as composite. In the latter case, therefore (*e.g.* in a mixed solution of æsculin and fraxin), the fluorescence is no longer characteristic. In substances which fluoresce in solution, the solvent exerts an influence, either on the intensity alone, or likewise on the nature of the fluorescence. Thus the aqueous solution of æsculetin-red exhibits a fluorescence different from that of the alcoholic solution. The fluorescence of some substances is strengthened, and sometimes also modified, by addition of acids, that of others by addition of alkalis. Solutions of æsculin, æsculetin, fraxin, and similar compounds, fluoresce more strongly on addition of ammonia or a fixed alkali; less strongly and in a different manner on addition of acids; in this latter case, the original fluorescence is restored by saturation with an alkali. The feeble fluorescence of neutral quinine salts is converted, by addition of most acids, into the strong and totally different fluorescence of the acid salts; but hydrochloric and hydriodic acids destroy it almost completely (V. Pierre, *Wien. Akad. Ber.* liii. (2. Abth.), 704; *Jahresb.* 1866, p. 79).

Fluorescence is developed in an aqueous solution of quinine by the addition of an oxygen-acid, such as sulphuric, phosphoric, nitric, iodic, acetic, benzoic, tartaric, &c., whereas hydracids, such as hydrochloric, hydriodic, hydroferrocyanic, hydroplatinocyanic, &c., not only do not develop fluorescence in the quinine solution, but destroy it when previously developed by an acid of the former class. Hyposulphurous acid resembles the hydracids in its effect on the fluorescence of a quinine solution; but this acid, though usually classed with the oxygen-acids, nevertheless exhibits many of the chemical characters of a hydracid (Stokes, *Chem. Soc. J.* [2] vii. 174). See Hyposulphurous Acid, under Sulphur.

According to C. B. Greiss (*Pogg. Ann.* cxxxiii. 171), fluorescent substances are found in all parts of plants and animals. Many organic compounds not occurring in nature (amyl alcohol, acetone, creosote) likewise exhibit weak fluorescence.

On the alteration of the fluorescence of certain vegetable tinctures, produced by filtration through animal charcoal, see J. E. Loughlin (*Sill. Am. J.* [2] xliii. 239; *Jahresb.* 1867, p. 104).

The conversion of rays of lower into rays of higher refrangibility—the opposite of the change which takes place in fluorescence—was designated by Emmsmann (*Pogg. Ann.* civ. 651 [1861]) as 'negative fluorescence.' An example of it is afforded by the incandescence of a platinum wire or of a piece of lime held in a hydrogen flame, the dark ultra-red rays which constitute the greater part of the spectrum of this flame being then converted into rays of higher refrangibility, and so becoming luminous. This phenomenon has been further studied by Akin (*The Reader*, Sept. 1863; *Phil. Mag.* [4] xxviii. 554; xxix. 28, 136) and Tyndall (*ibid.* xxviii. 329; xxix. 44, 218, 241; *Proc. Roy. Soc.* xiv. 33, 476). When the luminous and calorific rays from an electric lamp are passed through a sufficiently thick stratum of a solution of iodine in carbon bisulphide, which absorbs all the visible rays, and gives passage only to the invisible ultra-red rays, and these rays, which are the least refrangible of all, are then made to pass through a system of lenses, a focus of invisible but very hot rays is produced, which easily sets fire to inflammable substances, and raises metals and other solid bodies held in it to a state of vivid incandescence, causing them to emit rays of every degree of refrangibility (Tyndall). The same exaltation of refrangibility may be more simply exhibited by placing a piece of fluor-spar (chlorophane) in the flue of an ordinary stove, so that it may be heated by the dark rays radiated from the moderately hot walls of the flue; the mineral then becomes luminous in a few minutes (G. Bohn, *Jahresb.* 1867, p. 103). As fluorescence properly so called—*i.e.* the lowering of the refrangibility of rays—takes place at ordinary temperatures, whereas the phenomena just noticed, designated by Emmsmann as negative fluorescence, take place only at high temperatures, Tyndall prefers to denote them by the term calorescence. Akin uses the word calescence.

Circular Polarisation.—The rotatory power of volatile substances is not constant, but varies with the temperature, its variation being represented by the general formula $a + bt + ct^2$, in which c is very small and sometimes equal to nothing. For any given temperature, the rotations of the different rays are not exactly in inverse proportion to the wave-lengths, the variation being different in different substances. The proportion of the rotations of any *one* ray at different temperatures holds good likewise for all other rays, in the case of any given substance. This last law applies also to the vapours of camphor and certain volatile oils, the rotation of which is moreover the same in direction, and equal or nearly equal in amount to that which would be produced by the solid or liquid substance at the same temperature (Gernez, *Compt. rend.* lviii. 1108).

LIGHT, MEASUREMENT OF THE CHEMICAL ACTION OF. According to the method described on p. 689 of vol. iii. (which consists in the exact estimation of the tint which standard sensitive paper assumes when exposed for a given length of time to the action of daylight), a regular series of measurements was continued for two years at Kew Observatory (Roscoe, *Phil. Trans.* 1867, 555), proving that a continued series of such daily observations can be effectually and satisfactorily carried out. The curves (figs. 31, 32) show the rise and fall of monthly chemical intensity with the hour of the day at Kew for the year 1866, whilst the numbers in the following table give the mean monthly integrals of chemical intensity for the same period.

FIG. 31.

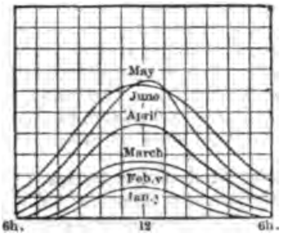
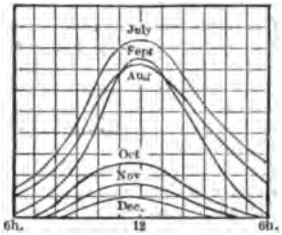


FIG. 32.



(*Light of the Intensity* 1·0 *acting for 24 hours* = 1,000.)

January .	15·0	May .	78·9	September .	70·1
February .	24·3	June .	92·3	October .	29·5
March .	34·5	July .	106·9	November .	15·6
April .	78·9	August .	94·5	December .	14·0

From these curves, as from the observational numbers, it is seen that the chemical intensity for hours equidistant from noon is the same. Thus

Chemical Intensity

The mean action, from 552 morning observations in 1865–67 at 9.41 A.M. is = 0·105.

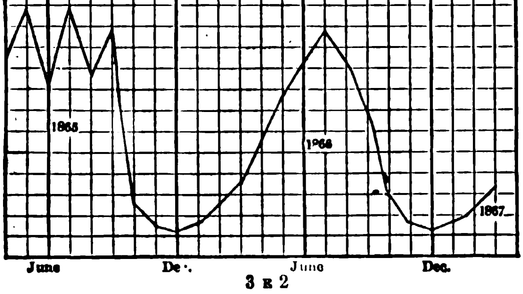
" " " 529 afternoon " " " 2.27 P.M. is = 0·107.

So that we may conclude that when the disturbing causes of cloud, &c., are eliminated, the daily maximum of chemical intensity corresponds to the maximum of sun's altitude, and that the chemical intensity exhibits no sign of a post-meridian maximum, as is observed in the measurements of hourly temperature. Although the curves of mean daily chemical intensity, showing the variation from hour to hour, are symmetrical, this relation appears by no means to hold good for the curves of yearly chemical intensity. This is distinctly seen by comparing the monthly means for the two months about the vernal with the two about the autumnal equinox, for 1865, '66, and '67:

1865, 7	Mean C. I.	1866	Mean C. I.
March 1867 . .	30·5	March 1866 . .	34·5
April 1865 . .	97·8	April 1866 . .	52·4
September 1865 .	107·8	September 1866 .	70·1
August 1865 .	88·9	August 1866 .	94·5

Or for 100 chemically active rays falling in the months of March and April 1865, '66, '67, at Kew, there fell, in the months of August and September 1865, '66, '67, 167 rays, the sun's mean altitude being the same in both cases. The curve (fig. 33) shows

FIG. 33.



the biennial variation of chemical intensity at Kew for the two years ending April 1, 1867. The yearly integral for the twelve months, January to March 1867, and April to December 1865, is 55·7 per diem, whilst that for the 12 months of 1866 is 54·7. From careful comparison of the other meteorological elements it appears that the difference in chemical intensity between spring and autumn cannot be ascribed to a greater amount of cloud at one of these seasons over that at the other, but rather to the variation in the transparency of the atmosphere, partly caused by variation in the humidity of the air, and partly by the presence of finely divided solid particles, which, floating about, produce the phenomenon of atmospheric opalescence.

Our knowledge concerning the distribution of the chemically active rays on the earth's surface is as yet but limited. It has been frequently stated (Golding Bird, *Nat. Phil.* 5th edit. 622) that the chemical intensity of light on snowy peaks and in tropical climates is much less than that in our own latitudes, and that photographers in Mexico have found it impossible, amidst the glaring rays of a tropical sun, to obtain a picture which, in the gloomier atmosphere of England, would need an exposure of only one minute.

A series of experiments made according to the above-described method (proposed by the writer of this article) by Dr. Thorpe at Pará on the Amazons (long. 48° 30′ W., lat. 1° 28′ S.) prove that any difficulties which a photographer may have in the tropics cannot be ascribed to an insufficient supply of the sun's chemically active rays. The following table gives the mean daily chemical intensities at Kew and Pará for 15 days in April 1866:

Date	Daily mean Intensity		Ratio
	Kew	Pará	
April 4, 1866 .	—	269·4	
" 6 " .	28·6	242·0	8·46
" 7 " .	7·7	301·0	39·09
" 9 " .	5·9	326·4	55·25
" 11 " .	25·4	233·2	9·18
" 12 " .	55·8	203·1	3·66
" 13 " .	52·2	337·8	6·46
" 14 " .	38·5	265·5	6·89
" 18 " .	39·8	350·1	8·80
" 19 " .	75·2	352·3	4·68
" 20 " .	38·9	385·0	9·90
" 23 " .	80·4	350·1	4·35
" 24 " .	83·6	362·7	4·34
" 25 " .	73·7	307·8	4·17
" 26 " .	89·1	261·1	6·67
Mean intensity . .	46·66	302·2	

The changes in chemical intensity, as observed from hour to hour, or even from minute to minute, are very sudden and remarkable. These sudden variations, seen in figs. 34, 35, 36, are caused by the passage of enormous thunder-clouds, which during the rainy season spread quickly over the sky; the chemical action sinks down to zero, and as the clouds pass away, with torrents of deluging rain, the chemical intensity again rises. If the observations made when the sun's disc was unobscured are tabulated, and a curve plotted from these numbers, we get a good idea of the march of daily chemical intensity under the equator during sunshine. This curve (fig. 36) is a symmetrical one, and exhibits a maximum at noon. The dotted line is the curve of mean chemical intensity for April at Kew, and the relation of the two intensities is as 52·4 to 313·3, or as 1 to 5·98.

A very exact series of experiments (Roscoe a. Thorpe, *Proc. Roy. Soc.* 1870, 301) has been subsequently made in Portugal, when the sky was cloudless, for the purpose of determining the relation existing between the sun's altitude and the chemical intensity of total daylight. This relation is shown to be graphically represented by a *straight line for altitudes above* 10°; this fact had previously been observed in a less complete way at Kew, Heidelberg, and Pará. Hence we learn that, although the chemical intensity for the same altitude at different places and at different times of the year varies according to the varying transparency of the atmosphere, yet the relation at the same place between altitude and intensity is always represented by a straight line. This variation in the direction of the straight line is due to the opalescence of the atmosphere, and it has been invariably observed that, for equal altitudes, the higher intensity is always found where the mean temperature of the air is greater, as in summer, when observations at the same place at different seasons are compared, or as the equator is approached, when the actions at different places are examined. The differences in the observed actions for equal altitudes (which may amount to more than 100 p. c. at different places, and to nearly as much at different seasons of the year) serve as exact measurements of (1) the transparency and (2) the reflecting power of the atmosphere.

FIG. 34.

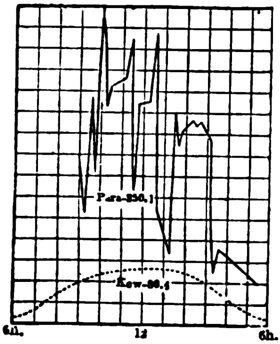


FIG. 35.

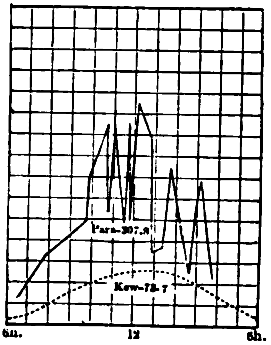
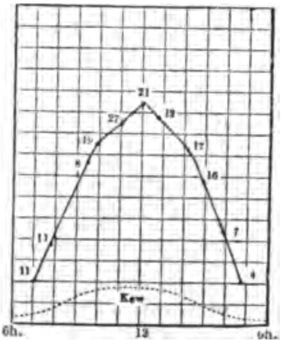


FIG. 36.



One important conclusion to which these determinations have led is the fact that at altitudes below 10° the direct sunlight is robbed of almost all its chemically active powers. This has been noticed in Manchester, Heidelberg, Kew, Pará, and Lisbon. Thus at Manchester, when the sun was 12° 3′ above the horizon, it was found that of 100 chemically active rays falling on the horizontal surface, less than 5 were due to the direct sunlight, whilst 95 came from the diffused light of the heavens, even when the sky was unclouded. At the same instant, of 100 rays of visible light as affecting the eye, 60 came directly from the sun, and only 40 from the diffuse sky-light. This same preponderance of the chemical activity of the diffuse light exists at higher altitudes. Thus at 25° 16′ the ratio of the chemical intensities of diffuse to direct sunlight was as 100 to 23, whilst the ratio of their visible intensities was as 100 to 400. The following table gives the results of the Lisbon experiments arranged according to the sun's altitude:

No. of Observations	Mean Altitude	Chemical Intensity		
		Sun	Sky	Total
15	9° 51′	0·000	0·038	0·038
18	19° 41′	0·023	0·063	0·085
22	31° 14′	0·052	0·100	0·152
22	42° 13′	0·100	0·115	0·215
19	53° 9′	0·136	0·126	0·262
24	61° 8′	0·195	0·132	0·327
11	64° 14′	0·221	0·138	0·359

This cutting off of the chemically active (most refrangible) rays is due to the *opalescence of the atmosphere* (Roscoe).

The small particles of floating solid and liquid matter which are seen dancing in the sunbeam, and are present in all natural air, reflect the blue rays and transmit the red, giving rise to the ruddy tints of sunrise and sunset. That mere traces of finely divided particles completely cut off the chemically active rays can be shown by a simple experiment. If we take a very slightly milky liquid, such as water containing $\frac{1}{10}$ of a grain of finely divided suspended sulphur in the gallon—which produces so slight an opalescence that we can scarcely detect it—and then endeavour to explode a bulb of mixed chlorine and hydrogen gases by a bright flash of light when the opalescent sextane required two months' treatment with potassium permanganate to oxidise it completely, yielding a mixture of fatty acids apparently containing caproic acid. Solid paraffin, melting at 56°, boiled for three or four days with sulphuric acid and potassium dichromate, with addition of a little manganese dioxide (which greatly facilitates the reaction), is converted mainly into cerotic acid, $C^{27}H^{54}O^2$, melting at 78°. The same paraffin heated with 5 or 6 vol. nitric acid diluted with 1½ vol. water, yielded a mixture of solid fatty acids, melting after purification at about 76°, and probably therefore containing cerotic acid, also volatile fatty acids, the most abundant of which was œnanthylic acid, while the nitric acid solution contained hydrocyanic acid, succinic acid, and an acid agreeing in composition and melting point with anchoic acid (Gill a. Meusel, *loc. cit.*).

Isomerism in the Paraffin Series.—These hydrocarbons are sometimes regarded as hydrides of the univalent alcohol-radicles C^nH^{2n+1}—methane, for example, as methyl-hydride, $H.CH^3$; ethane as ethyl hydride, $H.C^2H^5$. This view of their constitution is suggested by their formation by the action of water on the zinc-compounds of the same radicles; *e.g.*,

$$Zn(CH^3)^2 + 2H^2O = ZnH^2O^2 + \underset{\text{Methyl hydride}}{2(H.CH^3)};$$

and by the facility with which they give up one atom of hydrogen in exchange for chlorine and bromine, whereas the replacement of the remaining hydrogen-atoms is much more difficult. On the other hand, all these hydrocarbons, except methane, may be regarded as compounds of two atoms or half-molecules of alcohol radicles, C^nH^{2n+1}; thus

$$\underset{\text{Ethane.}}{C^2H^6} = \underset{\text{Ethyl hydride.}}{H.C^2H^5} \text{ or } \underset{\text{Dimethyl.}}{CH^3.CH^3}$$

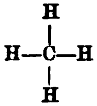
$$\underset{\text{Propane.}}{C^3H^8} = \underset{\text{Propyl hydride.}}{H.C^3H^7} \text{ or } \underset{\text{Methyl-ethyl.}}{CH^3.C^2H^5}$$

$$\underset{\text{Quartane.}}{C^4H^{10}} = \underset{\text{Quartyl hydride.}}{H.C^4H^9} \text{ or } \underset{\text{Diethyl.}}{C^2H^5.C^2H^5} \text{ or } \underset{\text{Methyl-propyl.}}{CH^3.C^3H^7}$$

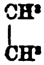
This latter view appears to accord with their formation by the action of zinc on the iodides of the alcohol-radicles, which is similar to that of hydrogen by the action of zinc on hydriodic acid; thus:

$$Zn + 2HI = ZnI^2 + HH.$$
$$Zn + 2C^2H^5I = ZnI^2 + C^2H^5.C^2H^5.$$
$$Zn + CH^3I + C^2H^5I = ZnI^2 + CH^3.C^2H^5.$$

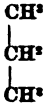
The first three hydrocarbons of the series however, viz. CH^4, C^2H^6, C^3H^8, exhibit exactly the same physical and chemical properties in whatever way they may be prepared; and indeed the constitutional formulæ of these bodies, viz.,



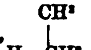
$$\begin{array}{c}H\\|\\H—C—H\\|\\H\end{array}$$



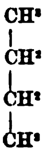
$$\begin{array}{l}CH^3\\|\\CH^3\end{array}$$



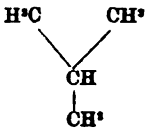
$$\begin{array}{l}CH^3\\|\\CH^2\\|\\CH^3\end{array}$$

show that they are not susceptible of isomeric modifications, inasmuch as there is but one way in which the carbon-atoms in either of them can be grouped; in ethane each carbon-atom is directly combined with three hydrogen-atoms and the other carbon-atom; and whether we regard it as ethyl hydride,  $\begin{array}{l}\;\;\;CH^3\\\;\;\;|\\H—CH^3,\end{array}$ or as dimethyl, $H^3C—CH^3$, this arrangement remains the same. In propane, C^3H^8, each carbon-atom is directly combined with at most two other carbon-atoms, and there is no other way in which the atoms can be arranged.

But if we look at the formula of the 4-carbon paraffin, C^4H^{10}, we see that it may be written in either of the following forms:



$$\begin{array}{l}CH^3\\|\\CH^2\\|\\CH^2\\|\\CH^3\end{array}$$



chloride solution. The relative sensitiveness of papers prepared in each of these solutions was accurately determined, and tables are given in which are found the relative times for which pieces of these papers must be exposed to a constant source of light in order to gain a given series of tints, and, therefore, the relative intensities of light to which they must be exposed for a constant time to gain the same series of tints. From this table the relative sensitiveness of any of these papers with respect to any tint can be calculated when their relative sensitiveness with respect to some one given tint is known. The following numbers give the relative sensitiveness of 5 papers with respect to the normal tint:

Chloride . .	1·000	Chlorobromide . .	4·022	Bromiodide . .	4·060
Chloriodide .	1·078	Bromide . . .	2·396		

Photometer for Photographic Purposes

H. Vogel (*Ber. d. deutsch. Chem. Ges.* 1868, 62) has described the arrangements of a simple photometer. It consists of a semi-transparent paper scale, of which the tints vary in regular gradation; under this scale is placed a paper sensitised with chromate of potash, which becomes darkened on exposure to light. In order to recognise the effect of the light, black letters are painted on the scale, and the portions of the paper under these letters remain unacted on. No numerical results of the working of this instrument have yet appeared.

Chemical Decomposition of the Vapour of Volatile Organic Bodies by the Action of Light.

Tyndall (*Proc. Roy. Soc.* xvii. 92, 223, 317; *ibid.* xviii. 176), by subjecting the vapours of volatile liquids to the action of concentrated sunlight, or to the concentrated beam of the electric light, has shown that a remarkable decomposition is brought about, which is rendered visible by the formation of singular cloud-like forms. These clouds disappear when the experimental tube through which the rays pass from end to end, is again rendered vacuous. The substance which was first experimented upon was nitrite of amyl (boiling from 91° to 96°); when the slightest trace of this vapour was introduced into the tube, and the electric beam allowed to shine through it, the tube at first appeared *optically empty*; nothing whatever was seen within it; but before a second had elapsed, a shower of liquid spherules was precipitated on the beam, thus generating a cloud within the tube. Dry oxygen, hydrogen, or nitrogen can be equally well used as a diluent, and the effect is, therefore, not due to any interaction between the nitrite and its vehicle. The seat of the observed action is in the vapour itself, but Tyndall does not attempt to determine strictly the character of the decomposition. Brown nitrous fumes were however noticed, and it is probable that amyl nitrate was formed. The more refrangible rays are those which especially produce these singular decompositions, though the effect was observed, but to a very much diminished degree, with the red rays. A solution of yellow chromate of potash, made of such a strength as to be identical in colour with that of the liquid nitrite of amyl, was found to stop the active rays more effectually than red glass; but by far the most complete mode of arresting the rays which produce these changes is to allow them to pass through a screen of the vapour of the nitrite itself: a layer of vapour ½ of an inch in thickness, although scarcely affecting the luminous intensity, was sufficient to absorb the whole of the chemical energy of the beam of the electric light. A blue cloud of decomposing nitrite of amyl can also be obtained by greatly diluting the vapour. Other organic liquids, such as iodide of isopropyl and iodide of allyl, as well as hydriodic acid, gave singularly beautiful cloud-forms of varying tints when subjected to a similar treament. H. E. R.

LIGNOSE. See Glycolignose (p. 640).

LIGNUM COLUBRINUM, said to be used with good results as a remedy for intermittent fever, contains a somewhat considerable proportion of brucine, together with a little strychnine (B. van Berlekom, *Zeitschr. f. Chem.* [2] ii. 443).

LINOLEIC ACID. $C^{16}H^{28}O^2$ (iii. 700).—The ethereal solution of the lead salt of this acid, left to evaporate on a glass plate, leaves a white amorphous residue consisting of the lead salt of oxylinoleic acid, $C^{16}H^{28}O^5$. The acid separated from this salt by hydrogen sulphide and dissolved in alcohol, remains on evaporation as a nearly colourless viscid mass, which becomes blood-red, but without alteration of composition, when heated to 100° or treated with acids or alkalis. Its colourless alcoholic solution is not altered by alkaline carbonates at the boiling heat, but caustic alkalis turn it red even at ordinary temperatures. When linoleic acid is exposed to the air in a thin film till its weight becomes permanent, a colourless resinous substance is formed, having the composition of a hydrate of oxylinoleic acid, $C^{16}H^{28}O^{5}.H^{2}O$. Heated to 100° it gives off 6·7 p. c. water, and becomes blood-red. By prolonged contact with the air, more quickly when frequently moistened with ether, colourless oxylinoleic acid loses its viscid consistence, and is converted into linoxyn, $C^{16}H^{27}O^{5\frac{1}{2}}$ or $C^{32}H^{54}O^{11}$, a neutral, amorphous, elastic, non-hygroscopic body, heavier than water, insoluble in water, dilute acids, alcohol, and ether, but soluble in a mixture of alcohol and chloroform. In warm aqueous potash, and more slowly in ammonia, it dissolves to a red liquid, which, when supersaturated with an acid, yields a yellowish-red flocculent precipitate, soluble in alcohol, and still more in ether, and exhibiting the composition and properties of oxylinoleic acid. Linoxyn is also formed in the drying of linseed or poppy oil exposed to the air (G. W. Mulder, *Scheikund. Verhandl. en Onderzoek.* iv. (1 Stuk), 1; *Jahresb.* 1865, p. 324).

LINOXYN. See the last article.

LINSEED OIL contains, according to Mulder (*loc. cit.*), 77·0 p. c. carbon, 11·2 hydrogen, and 11·8 oxygen. Besides linolein (about 80 p. c.), it contains elain (*i.e.* a fat yielding sebic acid by dry distillation), palmitin, and myristin (the two latter amounting to about 10 p. c. of the oil). By dry distillation it gives off sebic, palmitic, and myristic acids, together with acrolein, and leaves a substance insoluble in ether and resembling caoutchouc, from the analysis of which Mulder infers that it is an anhydride of linoleic acid, $C^{16}H^{27}O^{1\frac{1}{2}}$ or $C^{32}H^{54}O^{3}$.

LITHIUM. The following method of preparing a lithium salt from lepidolite is given by Mierzinski (*Zeitschr. f. Chem.* [2] v. 349). Twenty-five pounds of pulverised lepidolite are digested for twenty-four hours with 30 pounds of strong sulphuric acid, and then fused in a crucible till all excess of sulphuric acid is driven off. On exhausting the residual mass with hot water, the whole of the silica remains undissolved. The iron, manganese, and aluminium are precipitated from the solution by ammonium carbonate, and the sulphuric acid from the filtrate by barium chloride. The liquid, which contains only the chlorides of the alkali-metals, is evaporated to dryness; the residue is digested with alcohol, which dissolves only the lithium chloride; the syrupy lithium solution which remains on distilling off the alcohol is precipitated by ammonium carbonate; and the precipitate is washed with alcohol. See also Lunglmayr, *Dingl. pol. J.* clxxi. 293; *Jahresb.* 1863, p. 182;—Reichardt, *Dingl. pol. J.* clxxii. 447; *Jahresb.* 1864, p. 186;—Schrötter, *J. pr. Chem.* xciii. 27; also the article RUBIDIUM in this Dictionary, v. 128;—v. Hauer, *J. pr. Chem.* xcv. 148.

Rammelsberg (*Pogg. Ann.* cxxviii. 311; *Jahresb.* 1865, p. 167; 1866, p. 157) has examined the crystalline form and composition of several lithium salts, with the view of ascertaining whether they are isomorphous with the corresponding salts of potassium or sodium. The *sulphate*, $Li^{2}SO^{4} + H^{2}O$, crystallises in monoclinic prisms having the clinodiagonal, orthodiagonal, and principal axis in the proportion 0·8278 : 1 : 1·2021, and the angle of the inclined axes = 70° 29′. A solution of potassium sulphate and lithium sulphate in equivalent proportion, first deposits the former salt, then *potassio-lithic sulphate*, $KLiSO^{4}$, in double hexagonal pyramids having the secondary to the principal axis as 0·6006 : 1; they agree with the crystals of sodio-potassic sulphate only in their general symmetry, not in the ratio of their axes or the inclinations of their faces. The mother-liquor ultimately yields very small crystals having the form of the hydrated lithium sulphate above described, and the composition $(K^{2}SO^{4}.H^{2}O) + (4Li^{2}SO^{4} + H^{2}O)$ or $K^{2}Li^{8}(SO^{4})^{5} + 2H^{2}O$. A solution of the sulphates of lithium and sodium in equivalent proportions yields by evaporation hexagonal crystals (combinations of a rhombohedron having a terminal angle of 102° 28′ with the end-face and the second hexagonal prism). The first crop of these crystals had the composition $Na^{3}Li(SO^{4})^{2} + 6H^{2}O$, the second crop $Na^{4}Li^{2}(SO^{4})^{3} + 9H^{2}O$. Finally, crystals were obtained having the form of the hydrated lithium sulphate, but containing the sodium salt in isomorphous combination. The *hyposulphate*, $Li^{2}S^{2}O^{6} + 2H^{2}O$, obtained by decomposing barium hyposulphate with lithium sulphate, crystallises in rhombic combinations of prisms and pyramids having the axes $a : b : c$, as 0·5985 : 1 : 1·0355, isomorphous with the sodium salt. The crystals become moist in the air and dissolve very easily in water. The *neutral chromate*, $Li^{2}CrO^{4} + H^{2}O$, forms rhombic prisms having the axes $a : b : c$ as 0·6619 : 1 : 0·4663; very soluble in water. The *dichromate*, $Li^{2}CrO^{4}.CrO^{3} + 2H^{2}O$, γ. **Quintene, or amylene**, C^5H^{10} (or a compound isomeric with it), is formed by the action of zinc ethide on allyl iodide:

$$2C^3H^5I + Zn(C^2H^5)^2 = ZnI^2 + 2C^5H^{10}.$$

δ. **Sextene, or hexylene**, C^6H^{12}, is obtained in combination with hydriodic acid by the action of that acid on mannite:

$$\underset{\text{Mannite}}{C^6H^8(HO)^6} + 11HI = 6H^2O + 5I^2 + \underset{\substack{\text{Sextene}\\\text{hydriodide}}}{C^6H^{12}.HI};$$

and this hydriodide, heated with potassium hydrate, yields the hydrocarbon:

$$C^6H^{12}.HI + KHO = KI + H^2O + C^6H^{12}.$$

ε. **Quartene, or butylene**, C^4H^8, is obtained by precisely similar reactions from erythrite, $C^4H^6(OH)^4$.

Reactions.—1. The olefines are dyad radicles, uniting with 2 atoms of chlorine, bromine, &c., and with 1 atom of oxygen.

2. The chlorides, bromides, and other haloïd compounds of the olefines, treated with an alcoholic solution of *potash*, give up one atom of hydrogen and one atom of the haloïd element, yielding an olefine in which 1 atom of hydrogen is replaced by chlorine, bromine, &c., together with water and a haloïd salt of potassium; thus:

$$\underset{\substack{\text{Ethene}\\\text{bromide.}}}{C^2H^4Br^2} + KHO = KBr + H^2O + \underset{\text{Bromethene.}}{C^2H^3Br}$$

The resulting chlorinated, brominated, or iodated compound can, in its turn, take up 2 atoms of chlorine, bromine, or iodine, forming a body which can likewise give up hydrochloric, hydrobromic, or hydriodic acid, under the influence of alcoholic potash; the body thus formed can again take up 2 atoms of chlorine, bromine, or iodine, then give up HCl, HBr, or HI; and thus, by a series of perfectly similar reactions, we at length arrive at bodies consisting of the primitive olefine with all its hydrogen replaced by chlorine, bromine, or iodine, and the dichlorides, dibromides, and di-iodides of these last-mentioned bodies; thus from ethene may be derived the two following series of brominated compounds:

Ethene	C^2H^4	Ethene bromide . .	$C^2H^4Br^2$
Bromethene	C^2H^3Br	Bromethene bromide .	$C^2H^3Br\ .Br^2$
Dibromethene	$C^2H^2Br^2$	Dibromethene bromide .	$C^2H^2Br^2\ .Br^2$
Tribromethene	C^2HBr^3	Tribromethene bromide .	$C^2HBr^3\ .Br^2$
Tetrabromethene . . .	C^2Br^4	Tetrabromethene bromide	$C^2Br^4\ .\ .Br^2$

3. A monochlorinated or monobrominated olefine may give up the atom of chlorine or bromine which it contains, in the form of hydrochloric or hydrobromic acid, whereby it is reduced to a hydrocarbon of the following series: C^nH^{2n-2}. This reaction may take place at 130°–150°, under the influence of alcoholic potash, or, better, of sodium ethylate; thus:

$$\underset{\text{Bromethene.}}{C^2H^3Br} + C^2H^5NaO = NaBr + C^2H^5OH + \underset{\text{Ethine.}}{C^2H^2}$$

4. Ethene bromide and its homologues, treated with silver acetate or potassium acetate, exchange their bromine for an equivalent quantity of the halogenic residue of the acetate, $C^2H^3O^2$, giving rise to diatomic acetic ethers; thus:

$$\underset{\substack{\text{Ethene}\\\text{bromide}}}{(C^2H^4)''Br^2} + 2C^2H^3O^2K = 2KBr + \underset{\substack{\text{Ethene}\\\text{diacetate}}}{(C^2H^4)''(C^2H^3O^2)^2};$$

and these ethers, distilled with a caustic alkali, yield diatomic alcohols or glycols; for example:

$$\underset{\substack{\text{Ethene}\\\text{diacetate.}}}{(C^2H^4)''(C^2H^3O^2)^2} + 2KOH = 2C^2H^3O^2K + \underset{\substack{\text{Ethene}\\\text{alcohol.}}}{(C^2H^4)''(OH)^2}$$

5. The bromides $C^nH^{2n}Br^2$, heated to 275° with a mixture of potassium iodide, copper, and water, give up their bromine and reproduce the original olefine, together with other hydrocarbons (p. 707).

6. Some olefines, when briskly shaken up with strong sulphuric acid, unite with it, forming acid ethers of sulphuric acid, which contain the monatomic alcoholic radicles corresponding to the olefines; thus:

$$C^2H^4 + SO^4H^2 = SO^4.C^2H^5.H:$$

M

MACHROMIN. See the next article.

MACLURIN. $C^{13}H^{10}O^{6}$. *Morintannic Acid* (iii. 1049) (Hlasiwetz a. Pfaundler, *J. pr. Chem.* xciv. 65; *Jahresb.* 1864, p. 558).—A moderately concentrated solution of this substance boiled with sulphuric acid and zinc, becomes deep red and ultimately yellow, and then contains, together with phloroglucin, a substance which, from its variations of colour, is called machromin. To separate this substance, the yellow liquid decanted from the zinc is mixed with ⅓ vol. alcohol, and agitated with ether as long as the latter becomes coloured; the ethereal solution is evaporated; and the residue diluted with water is precipitated with lead acetate, the phloroglucin then remaining in solution. The yellowish precipitate, which quickly becomes green on exposure to the air, is decomposed with hydrogen sulphide; the lead sulphide is washed with boiling dilute alcohol; the resulting liquid is evaporated in a vacuum; and the granular crystalline mass thereby separated is repeatedly crystallised from boiling dilute alcohol.

Machromin thus obtained forms colourless crystalline spangles, appearing under the microscope as tufts or stars of slender needles, very sparingly soluble in water and in alcohol, somewhat more easily in ether. The crystals exposed to air and light, or dried by heat, gradually acquire a dark blue colour. The hot-prepared aqueous solution also acquires a deep violet-blue colour on exposure to the air, and then yields with hydrochloric acid an amorphous indigo-blue precipitate; ferric chloride produces (best in a very dilute alcoholic solution) a violet-red colour, afterwards changing to blue; the solution of machromin in dilute ammonia, or a caustic fixed alkali, likewise turns blue on exposure to the air. Silver nitrate and mercuric chloride produce a violet coloration, the former with reduction of the metal. An alkaline cupric solution is also reduced by heating with machromin. The solution of machromin in strong sulphuric acid is orange-red at first, then becomes yellow, and after warming (or dilution) emerald-green, and after supersaturation with alkalis, violet.

Hlasiwetz a. Pfaundler give, as the most probable expression of the composition of machromin, the formula $C^{14}H^{10}O^{5}.3H^{2}O$, and suppose it to be formed from protocatechuic acid (resulting from decomposition of the maclurin), according to the equation:

$$2C^{7}H^{6}O^{4} + H^{4} = C^{14}H^{10}O^{5} + 3H^{2}O.$$

Machromin is not however produced by the action of nascent hydrogen on ready-formed protocatechuic acid.

When a solution of maclurin in 10 pts. water is heated with sodium-amalgam, and the resulting yellow liquid is saturated with sulphuric acid, keeping it as much as possible excluded from the air, it yields to ether, on agitation, phloroglucin and an amorphous substance, which has nearly the composition $C^{14}H^{12}O^{5}$, and may therefore also be formed from protocatechuic acid by addition of hydrogen: $2C^{7}H^{6}O^{4} + H^{6} = C^{14}H^{12}O^{5} + 3H^{2}O$. This compound is soluble in water and in alcohol; easily turns brown; is precipitated by lead acetate; forms with ferric chloride a grass-green liquid, turning red on addition of sodium carbonate; reduces silver solutions and alkaline cupric solutions; and yields by dry distillation crystals having the composition of pyrocatechin.

Acetyl-maclurin, $C^{13}H^{9}(C^{2}H^{3}O)O^{6} + 1\frac{1}{2}H^{2}O$, is formed by heating maclurin to 100° in a sealed tube with acetyl chloride. It is a viscid oil, precipitated by water from the alcoholic solution.

MAGNESIUM. From experiments by Woods (*Phil. Mag.* [4] xxx. 49), the calorific equivalent of magnesium appears to be higher than that of any other metal. The oxidation of 1½ grm. magnesium develops heat sufficient to raise the temperature of 1,000 grms. of water 10·67°, whereas the heat produced by oxidation of an equivalent quantity of zinc raises it by only 5·35°, and of an equivalent quantity of potassium or sodium, 9·72°. The quantities of heat produced by the combination of equivalent quantities of zinc, potassium, and magnesium are as the numbers 6·42, 12·78, and 14·0, or as 1 : 1·99 : 2·17. According to Ditte (*Compt. rend.* lxxiii. 108), the calorific equivalents of zinc and magnesium are as 1 : 1·61.

Magnesium in the finely divided state unites at determinate temperatures with sulphur, phosphorus, and arsenic, and at a red heat decomposes the oxides of carbon, sulphurous oxide, most metallic oxides, and many hydrocarbons (Parkinson, *Chem. Soc. J.* [2] v. 125). According to Phipson (*Proc. Roy. Soc.* xiii. 217), iodine and sulphur may be distilled over magnesium without altering it; silica and boric oxide are easily reduced by it; from sodium carbonate at a red heat it separates a large quantity of carbon. Ammonia and the fixed caustic alkalis do not act upon it at ordinary temperatures. It precipitates nearly all metals from their neutral solutions (even iron and manganese from ferrous and manganous salts) in the metallic state; aluminium and uranium, and perhaps also chromium, as oxides. Roussin (*J. Pharm.* [4] iii. 413) regards magnesium as particularly well adapted for the precipitation of poisonous metals in toxicological investigations, and is of opinion that it might be advantageously used as a substitute for zinc in voltaic combinations, on account of its great electromotive power. On the precipitation of metals by magnesium, see also Commaille (*Bull. Soc. Chim.* [2] vi. 257; *Jahresb.* 1866, p. 171).

Reactions of Magnesium Salts.—According to Pribram (*Jahresb.* 1866, p. 174), the ordinary statement that only half the magnesia is precipitated from magnesium salts by excess of *ammonia* is erroneous, 58 p. c. being immediately precipitated, 61 p. c. after three hours, and from 84 to 92 p. c. after fifteen hours.

According to R. Warington (*Chem. Soc. J.* [2] iii. 27), magnesia is dissolved by the *salts of the fixed alkalis*, as well as by ammonia, though in much smaller quantity. Hence the precipitation of ammonia by fixed alkalis is never complete, unless a very large excess of the precipitant is used. The clear solution obtained by mixing a magnesium salt with ammonia and the exact quantity of ammoniacal salt required to prevent precipitation, deposits magnesia on dilution with water, whereas addition of strong ammonia within certain limits causes no precipitation. This appears to be the cause of the turbidity produced when the clear slightly ammoniacal wash-water of ammonio-magnesian phosphate runs into a filtrate containing a considerable quantity of magnesia.

Potassium sulphide and *sodium sulphide* added to solutions of magnesium salts, precipitate magnesium hydrate and form a sulphydrate of the alkali-metal:

$$MgCl^2 + 2Na^2S + 2H^2O = 2NaCl + 2NaHS + MgH^2O^2.$$

A solution of 1 pt. magnesium chloride in 6,000 pts. water is immediately and distinctly clouded by sodium sulphide, the precipitate being soluble in excess of the magnesium salt (Pelouze, *Jahresb.* 1866, p. 174).

Fresenius (*Zeitschr. anal. Chem.* vii. 310) confirms his former observation, that in separating calcium from magnesium by means of ammonium oxalate, it is necessary to redissolve the precipitated calcium oxalate in hydrochloric acid, and reprecipitate with ammonia and ammonium oxalate, inasmuch as the first precipitate always carries down with it a certain quantity of magnesium salt.

On the separation of magnesia from the alkalis by means of ammonium phosphate (iii. 754), see further Reynoso (*Compt. rend.* lvi. 873; *Jahresb.* 1863, p. 675); Chancel (*ibid.* 1866, p. 796).

Alloys of Magnesium.—With *potassium* and *sodium*, magnesium forms malleable alloys, which decompose water at ordinary temperatures: 15 pts. magnesium and 85 pts. *tin* form a hard brittle lavender-coloured alloy, which decomposes water like the preceding. *Mercury* does not amalgamate with magnesium at ordinary temperatures (Phipson, *Proc. Roy. Soc.* xiii. 217). Alloys of magnesium and *thallium* are formed by melting the two metals together in any proportions, and may be drawn out into wire or ribbon. The alloy containing 5 p. c. thallium is stable, and more malleable than magnesium; those containing larger proportions of thallium oxidise more readily. All these alloys burn less quickly and less brightly than pure magnesium; the flame is smaller, and of a pure white colour even when the alloy contains 50 p. c. thallium (S. Mellon, *Chem. News*, xv. 245).

Parkinson (*Chem. Soc. J.* [2] v. 125) has prepared a considerable number of magnesium alloys, by fusing the metals together in a glass tube in a stream of hydrogen, or on a larger scale, and with the less fusible metals, by fusion in an earthen crucible under a flux composed of equal parts of fluor-spar and cryolite, or of 1 pt. of fluor-spar and 2 pts. sodium chloride, the magnesium, on account of its small specific gravity, being attached to the end of an iron rod and stirred into the fused metal. In this manner alloys have been obtained with sodium, aluminium, cadmium, zinc, lead, bismuth, tin, antimony, mercury, silver, gold, and platinum; also triple alloys of magnesium with bismuth and copper, with copper and gold, and with copper and nickel. Iron, cobalt, and nickel do not appear to form alloys with magnesium; zinc, only by fusion in hydrogen; aluminium, only by fusion in a crucible lined with magnesia. All these alloys are very brittle, somewhat harder than the component metals, resemble them in colour, and have a granular or crystalline fracture; they appear to be too easily alterable to be available in the arts. An *arsenide of magnesium* is formed by slowly heating 3 pts. magnesium-filings and about 6·2 pts. arsenic to dull redness in a stream of hydrogen; it has a chocolate-brown colour, faint metallic lustre, and fine-grained fracture, is very brittle, very difficult to fuse, and quickly crumbles to a brown powder on exposure to the air (Parkinson).

Magnesium Fluoride.—The slag obtained in heating magnesium with sodium silicofluoride (*infra*) leaves, when exhausted with boiling water, a sodio-magnesic fluoride, $NaF.MgF^2$, crystallised in cubes resembling common salt; they are contaminated with free silicon, but may be purified by treatment with a mixture of hydrofluoric and nitric acids. The same double fluoride is obtained by fusing magnesium chloride with excess of sodium fluoride and chloride (Geuther, *Jahresb.* 1865, p. 173); also in the amorphous state by boiling a solution of sodium fluoride with magnesia: $3NaF + MgH^2O^2 = 2NaHO + NaF.MgF^2$ (Tissier, *Compt. rend.* lvi. 848).

Oxides.—Magnesia, prepared by igniting the nitrate, is converted by prolonged immersion in water into a hydrate, MgH^2O^2, having the density and toughness of marble, but harder and more translucent. A hydrate having the same properties, but containing also alumina, ferric oxide, magnesium carbonate, and sand, is obtained by the action of water on the residue left on igniting commercial magnesium chloride. Pure magnesia possesses the property of hardening with water only when prepared by igniting the nitrate or chloride at a moderate red heat; by exposure for 12 hours to a white heat, it loses this property altogether. Magnesia prepared from the basic carbonate yields under similar circumstances a hydrate having only the hardness of talc (H. Sainte-Claire Deville, *Compt. rend.* lxi. 975). According to H. Schwarz (*Bull. Soc. Chim.* [2] ix. 78), magnesia prepared by igniting native magnesite ($MgCO^3$) at the lowest possible temperature, exhibits the hydraulic properties of the hydrate obtained as above by Deville. The paste prepared from it with water hardens in about twelve hours, afterwards withstands the action of water, and by prolonged immersion therein, acquires the hardness of the best Portland cement. According to Sorel (*Compt. rend.* lxv. 102), a mixture of magnesia with a concentrated solution of magnesium chloride (of sp. gr. 1·16 to 1·26) hardens in a short time to a compact mass of hydrated basic chloride, which resists the action of water. The pasty mixture is very plastic, and capable of binding more than twenty times its weight of sand or other inert powders. Cements or mortars of similar character may be prepared with other chlorides, especially chloride of calcium.

A *suboxide of magnesium* appears to be formed when a solution of sodium or ammonium chloride is electrolysed with poles formed of magnesium wire, the positive pole becoming covered with a black deposit, which exhibits the characters of an oxide (W. Beetz, *Pogg. Ann.* cxxvii. 43; *Jahresb.* 1866, p. 172).

Phosphide.—When melted phosphorus is made to flow upon magnesium-filings heated to dull redness in a stream of hydrogen, combination takes place attended with vivid combustion. The same compound is obtained by heating magnesium-filings with red phosphorus in a narrow-necked flask. It forms a very hard brittle mass, not fusible even at a red heat; has a dark brown colour; and exhibits a semi-metallic lustre on its crystalline fracture. It decomposes water and hydrochloric acid, with evolution of hydrogen phosphide; is permanent in dry air, but is decomposed by moist air in the same manner as by water. Its composition is represented by the formula P^2Mg^3 (Parkinson, *Chem. Soc. J.* [2] v. 309). F. P. Blunt (*ibid.* iii. 106), by passing phosphorus-vapour over magnesium-filings heated to dull redness in a stream of carbon dioxide, obtained a black coherent mass, which was not attacked by dilute hydrochloric acid, scarcely by dilute sulphuric acid, and very slowly even by hot nitro-muriatic acid; when intimately mixed with metallic magnesium, however, it was decomposed by hydrochloric acid, with copious evolution of hydrogen phosphide. Parkinson regards this black product as a mixture of charcoal and magnesia with only a small quantity of magnesium phosphide, inasmuch as magnesium is scarcely attacked at a dull red heat by phosphorus-vapour, which, however, easily decomposes carbon dioxide at that temperature.

Silicide. Mg^4Si^3 (?).—This compound, first obtained by Wöhler (v. 266), is prepared by strongly igniting sodium silicofluoride with magnesium in a crucible filled up with common salt, and may be purified from unaltered magnesium by boiling with solution of sal-ammoniac, and from adhering silica by friction on smooth paper and levigation. It forms lead-grey crystals, apparently regular octohedrons, heavier than water. It is

HYDROCARBOSTYROL. $C^9H^9NO = (C^6H^4)''\left\{\begin{matrix}(NH)''\\(C^3H^4O)''\end{matrix}\right.$ (Buchanan a. Glaser, *Zeitschr. f. Chem.* [2] v. 194).—A body produced by reduction of nitrophenyl-propionic acid in the same manner as carbostyrol or carbostyryl from nitrocinnamic acid (i. 802). It has the composition of amidophenyl-propionic acid, $C^9H^{11}NO^2$, *minus* H^2O. To prepare it, nitrophenyl-propionic acid is treated with tin and hydrochloric acid, and the crystals which separate from the diluted and filtered liquid are recrystallised several times from alcohol. It is a very stable substance, melting at 160°, and distilling without decomposition at a higher temperature. In its chemical relations it resembles the amides. It dissolves easily in warm concentrated hydrochloric or hydrobromic acid, apparently forming definite compounds, which, however, decompose spontaneously even in the cold. Potash and soda dissolve it but slowly even at the boiling heat; it is nearly insoluble in water, moderately soluble in alcohol and ether.

HYDROCINNAMIC ACID. See CINNAMIC ACID (p. 468).

HYDROCITRIC ACID. See CITRIC ACID (p. 473).

HYDROCOMENIC ACID, $C^6H^6O^5$, is produced by the action of sodium-amalgam on comenic or bromocomenic acid. It is a yellowish, strongly acid, syrupy liquid forming a white silver salt, $C^6H^4Ag^2O^5$, easily reduced by heat (J. v. Korff, *Ann. Ch. Pharm.* cxxxviii. 191).

HYDROCOUMARIC or **MELILOTIC ACID.** $C^9H^{10}O^3$ (Zwenger a. Bodenbender, *Ann. Ch. Pharm.* cxxvi. 257; Zwenger, *ibid. Suppl.* v. 100; *Jahresb.* 1867, p. 439). This acid occurs, combined with coumarin, in the yellow melilot (*Melilotus officinalis*), forming the compound $C^{18}H^{16}O^5 = C^9H^{10}O^3 . C^9H^6O^2$, which may be called melilo-coumarin. (See COUMARIN, p. 499.) When the aqueous decoction of the plant, evaporated to the consistence of a thin extract, is treated with ether as long as the ether acquires an acid reaction, and the green mass which remains after distilling off the ether is repeatedly boiled with a large quantity of water, well-defined crystals of melilo-coumarin separate on cooling. The solution of these crystals (or the aqueous decoction of the extract above mentioned) is mixed with basic lead acetate, carefully avoiding an excess, which would exert a solvent action; and the precipitate which forms after long standing is collected on a filter, washed first with cold water, then with alcohol and ether to remove free coumarin, and repeatedly boiled with water, as long as the hot filtrate deposits a crystalline precipitate of lead hydrocoumarate. This precipitate decomposed by hydrogen sulphide yields hydrocoumaric acid, which may be purified by repeated precipitation with neutral lead acetate: 100 pounds of the plant yield from 1½ to 2 ounces of the pure acid.

Hydrocoumaric acid may be produced synthetically from coumarin by gradually adding sodium-amalgam to an aqueous solution of that substance containing a little alcohol, each portion of sodium-amalgam being added only after the alkaline reaction produced by the preceding portion has nearly disappeared. By this treatment the coumarin, in the course of a few days, is almost wholly converted into hydrocoumaric acid, which may be precipitated by lead acetate. On boiling the precipitate with water, the greater part, consisting of lead hydrocoumarate, dissolves, while a small quantity of coumarate remains behind, showing that the coumarin, $C^9H^6O^2$, has first been converted, by addition of the elements of water, into coumaric acid, $C^9H^8O^3$, which has then been converted into hydrocoumaric acid by addition of 2 at. hydrogen.

Hydrocoumaric acid dissolves in 20 pts. water at 18°, in less than 1 pt. at 40°, very easily also in alcohol and ether. From a hot-saturated aqueous solution it crystallises, after long standing at ordinary temperatures, in spicular arragonitic crystals an inch long. It melts at 82°; solidifies in the crystalline state on cooling; has a strong acid reaction, a sour astringent taste, an aromatic honey-like odour; decomposes carbonates with facility; and dissolves zinc and iron when heated, with elemination of hydrogen. Its solution in excess of ammonia, when exposed to the air, gradually acquires an indigo-blue colour, becoming reddish when the liquid is heated. On adding the aqueous solution by drops to dilute *ferric chloride*, a bluish coloration is produced, which gradually disappears, with formation of a yellowish precipitate. *Chloride of lime* colours the solution yellow and red when heated. By fusion with *potash*, hydrocoumaric acid is resolved, with evolution of hydrogen, into salicylic and acetic acids:

$$C^9H^{10}O^3 + 2H^2O = C^7H^6O^3 + C^2H^4O^2 + 2H^2.$$

The *metallic hydrocoumarates* are for the most part easily crystallisable; those of the alkali-metals and alkaline earth-metals have a slight alkaline reaction, the ammonium salt and the salts of the heavy metals an acid reaction. The less soluble salts are obtained by precipitation; the more soluble by neutralisation of the corresponding dibromosuccinic acid) is liquid and boils at 212°. The barium and silver salts of bromomaleic acid crystallise in needles; the latter dissolves easily in water without decomposition, and is but slowly decomposed by boiling in ammoniacal solution.

The two bromomaleic acids above described are also formed, together with dibromosuccinic and isodibromosuccinic acids and bromoform, when phenaconic acid is heated with bromine and a quantity of water smaller than that which was used in the experiments above described. (See PHENACONIC ACID.)

Chloromaleic acid, $C^4H^3ClO^4$, apparently identical with that described by Perkin a. Duppa (iii. 788), is obtained by the action of baryta-water on an amorphous chlorinated acid formed, together with trichlorophenomalic acid, by the action of chlorous acid on benzene. (See PHENOMALIC ACID.) It is separated from the resulting solution—after removal of baryta and hydrochloric acid—by half neutralising with potash, leaving the acid potassium salt to crystallise, and decomposing this salt with an acid; and is finally purified by recrystallisation. The chloromaleic acid thus obtained crystallises in groups of small white needles, easily soluble in water, alcohol, and ether, and melting at 171°–172°. By prolonged fusion, especially at 180°, it is resolved into water and an oily anhydride which is reconverted into the acid by contact with water. Chloromaleic acid is reduced by hydriodic acid to ordinary succinic acid. It is bibasic; the neutral chloromaleates of alkali-metal are easily soluble in water. The acid potassium salt, $C^4H^2ClKO^4 + H^2O$, forms hard crystals; the barium salt, $C^4HClBaO^4 + 5H^2O$, chalky crusts composed of small laminæ. The soluble salts form with ferric chloride a white flocculent precipitate, with lead acetate a white amorphous precipitate $= C^4HClPbO^4$, and with silver nitrate a white microscopically crystalline precipitate $= C^4HClAg^2O^4$ (Carius, *Deut. Chem. Ges. Ber.* 1870, 334).

MALIC ACID. $C^4H^6O^5$.—This acid exists, according to Gintl (*Zeitschr. f. Chem.* [2] v. 377), in the leaves of the common ash. Reinsch (*ibid.* [2] 221) recommends the preparation of it from the fruits of the common sumach (*Rhus coriaria*). The expressed cold aqueous infusion of these leaves, precipitated with lead acetate and then boiled, yields a large quantity of lead malate. Crystallised calcium malate may also be obtained by boiling the juice with chalk, and evaporating the still acid solution.

Malic acid treated with *sodium* in alcoholic solution is converted into an acid resembling hydrocitric acid (p. 473), the calcium salt of which has the composition $C^4H^6CaO^5 + 2\frac{1}{2}H^2O$ (Kämmerer, *Jahresb.* 1866, p. 403).

Neutral potassium malate subjected to *electrolysis* is decomposed as follows: *a.* Fundamental reaction: $C^4H^4O^5K^2 = C^4H^4O^4 + O + K^2$.—*b.* Part of the anhydride $C^4H^4O^4$ is reconverted into malic acid; another portion is oxidised, yielding aldehyde and carbon dioxide: $C^4H^4O^4 + O = C^2H^4O + 2CO^2$.—*c.* Acetic acid is formed as a secondary product. A mixture of 4 mol. of the neutral malate with 1 mol. potassium hydrate yields the same products. Free malic acid is for the most part converted into aldehyde and carbon dioxide (Burgoin, *Bull. Soc. Chim.* [2] ix. 429).

Dry malic acid heated in the water-bath for three or four days with an equal volume of cold-saturated aqueous *hydrobromic acid* is converted into monobromosuccinic acid:

$$C^4H^6O^5 + HBr = H^2O + C^4H^5BrO^4.$$

With a larger quantity of fuming hydrobromic acid, the malic acid is converted at 100° into fumaric acid, $C^4H^4O^4$, and at 110°–120° carbon dioxide and carbon monoxide are formed by more complete decomposition (Kekulé, *Ann. Ch. Pharm.* cxxx. 11).

Detection and Separation of Malic Acid.—1. Malic acid in the free state may be recognised by evaporating its aqueous solution in a test-tube, and then heating the tube in a sand-bath to 160°–170° till the crystalline sublimate no longer increases; the maleic or fumaric acid thus produced may be recognised by its usual characters.—2. Calcium malate precipitated by alcohol from a solution of malic acid mixed with calcium chloride, shrinks together when the liquid is warmed, and forms on cooling a mass easily pulverised by pressure. As the solution with the precipitate bumps very violently when heated, it is best to pour off the alcohol, dissolve the precipitate in water, boil the solution, and mix it with pure alcohol.—3. The well-known lead reaction (iii. 791) is for the most part best exhibited by liberating the malic acid from its salts, and then precipitating it with lead acetate. It is only when lead malate is present in a liquid unmixed with other salts that it exhibits the characteristic reaction when heated.—4. When a solution containing free malic acid is neutralised with magnesia, and the filtered solution is mixed with alcohol, a precipitate of magnesium malate is obtained, which behaves like the calcium salt when heated (Barfoed, *Zeitschr. anal. Chem.* [2] v. 402).

Separation from other acids.—Malic acid may be detected, in presence of *oxalic* of the acid $C^7H^6O^3$, by the relative position of the groups OH and $C^3H^5O^2$ in the benzene nucleus; thus:

Ortho-series.	Meta-series.	Para-series.
1 : 2	1 : 3	1 : 4
Oxybenzoic.	Salicylic.	Para-oxybenzoic.
Phloretic.	Hydrocoumaric or melilotic.	Hydropara-coumaric.

Hydroparacoumaric acid has been obtained synthetically from phenyl-propionic or hydrocinnamic acid (p. 468) as follows. This acid treated with strong nitric acid yields *nitrophenyl-propionic acid*, $C^6H^4\left\{\begin{matrix}NO^2\\C^3H^5O^2\end{matrix}\right.$, which when oxidised by chromic acid is completely converted into nitrodracylic acid, and therefore belongs to the para-series. Nitrophenyl-propionic acid treated with tin and hydrochloric acid is converted into *amidophenyl-propionic acid*, $C^6H^4\left\{\begin{matrix}NH^2\\C^3H^5O^2\end{matrix}\right.$ (together with hydrocarbostyrol, p. 715); the hydrochloride of this amidated acid dissolved in absolute alcohol and treated with nitrous acid is converted into *diazophenyl-propionic chloride*, $C^9H^8N^2O^2.HCl$ or $C^6H^4\left\{\begin{matrix}N{\equiv}NCl\\C^3H^5O^2\end{matrix}\right.$; and by boiling the solution of this compound, whereby nitrogen is evolved, removing the chlorine by lead carbonate, the lead by hydrogen sulphide, and evaporating, *oxyphenyl-propionic acid*, $C^6H^4\left\{\begin{matrix}OH\\C^3H^5O^2\end{matrix}\right.$, is deposited in yellowish crystals. The acid thus obtained agrees in all its properties with the hydroparacoumaric acid obtained by Hlasiwetz a. Malin, excepting that its solution mixed with ferric chloride forms a blue liquid which soon becomes milky and deposits a resinous substance, the filtered liquid still retaining its blue colour. Its cold-saturated solution mixed with a few drops of strong nitric acid becomes red, then milky, and after a few hours deposits long needles of a nitro-compound, which dissolve in ammonia with deep red colour. The acid becomes milky when mixed with bromine-water, and reduces an alkaline cupric solution at the boiling heat (Buchanan a. Glaser, *Zeitschr. f. Chem.* [2] v. 193). See PROPIONIC ACID.

HYDROCYANOBENZIDE. See HYDROBENZAMIDE (p. 703).

HYDROCYANO-ROSANILINE. See ROSANILINE.

HYDROCYANOSALIDE. See HYDROSALICYLAMIDE (p. 721).

HYDRO-EUTHIOCHROIC ACID. See DERIVATIVES OF TETRACHLOROQUINONE, under QUINONE.

HYDROGEL. The name applied by Graham to the gelatinous hydrate of a colloïdal substance. (See COLLOÏDAL ACIDS, v. 1088.)

HYDROGEN. The evolution of hydrogen by the action of zinc on hydrochloric acid, or of sodium-amalgam on water, is considerably diminished when the reaction takes place under pressure, as in sealed tubes (Cailletet, *Compt. rend.* lxviii. 395). Berthelot (*ibid.* 536) regards the diminution of chemical action in this and similar cases, not as a direct consequence of the increased pressure, but as due to the formation of a layer of saturated solution on the surface of the metal, the removal of this layer by agitation or diffusion being retarded when the reaction takes place under pressure, in consequence of the diminished size of the gas-bubbles; moreover, part of the hydrogen eliminated at the beginning of the reaction remains adhering to the surface of the metal and protects it from the action of the acid, and this gaseous layer is of course less able to escape when the liquid is subject to increased pressure.

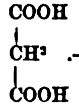
The salts of *ammonia*, *methylamine*, *ethylamine*, *aniline*, *naphthylamine*, and probably other amine-bases, give off hydrogen when zinc is immersed in their aqueous solutions, the reaction taking place even at ordinary temperatures, but more readily at 40°. Iron acts in the same manner, but less strongly. With zinc and iron, an ammonium salt, and free ammonia, the evolution of gas is as rapid as with zinc and dilute sulphuric acid. Ammonia nitrate, however (and probably also the nitrates of the alcoholic ammonias), forms an exception to the general rule, inasmuch as it does not evolve hydrogen, but nitrogen monoxide, when heated to 50° in contact with zinc (Lorin, *Compt. rend.* lx. 745).

On the passage of hydrogen through metals at a red heat, and its absorption by metals, especially by palladium, see GASES, ABSORPTION OF (p. 634). From the properties of the hydrogenised palladium, Graham infers that it is a true metallic alloy, and that the hydrogen enters into it as a metal, which he designates as deliquescent, strongly acid substance, which becomes brown at 100°, and gives off stinking vapours at higher temperatures. The solution of the acid is not precipitated by barium acetate, and only imperfectly by lead acetate. The barium salt, $C^4H^4BaO^6S$, is obtained, by supersaturating the acid with baryta-water, as a flocculent precipitate somewhat soluble in water. The *lead salt* is soluble in acetic acid. The *silver salt*, $C^4H^4Ag^2O^6S$, is a white precipitate which easily turns black. When a solution of sulphomalic acid in 20 pts. water is carefully evaporated with excess of nitric acid, sulphosuccinic acid, $C^4H^6O^7S$, is formed, together with small quantities of oxalic and sulphuric acids (Carius, *Ann. Ch. Pharm.* cxxix. 6).

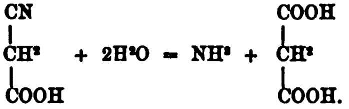
MALOBIURIC ACID. $C^5H^5N^3O^4 = N^3\begin{cases}(CO)^{2\prime\prime} \\ (C^3H^2O^2)'' \\ H^3\end{cases}$.—An acid analogous in constitution and mode of formation to biuret, $N^3(CO)^2H^4$, produced as an ammonium salt by heating barbituric acid to 150°–170° with urea:

$$\underset{\text{Barbituric acid.}}{C^4H^4N^2O^3} + \underset{\text{Urea.}}{CH^4N^2O} = \underset{\text{Ammonium malobiurate.}}{C^5H^4(NH^4)N^3O^4}$$

The acid is prepared by dissolving the crude ammonium salt in potash and supersaturating the solution with hydrochloric acid, and purified by repeating this treatment several times. It is distinguished from dibarbituric acid (the product of the action of heat on barbituric acid) by its granular character, by its greater solubility in water, and by dissolving completely when treated with bromine and water, instead of yielding a yellow bromide (v. 962). Nitric acid converts it into dilituric acid. Its salts are amorphous or finely crystalline precipitates (Baeyer, *Ann. Ch. Pharm.* cxxxv. 312).



MALONIC ACID. $C^3H^4O^4 = \begin{array}{l}COOH \\ | \\ CH^2 \\ | \\ COOH\end{array}$.—The formation of this acid from cyanacetic acid (or cyanacetic ether, iii. 799) is represented by the equation:



$$\begin{array}{l}CN \\ | \\ CH^2 \\ | \\ COOH\end{array} + 2H^2O = NH^3 + \begin{array}{l}COOH \\ | \\ CH^2 \\ | \\ COOH.\end{array}$$

It is also produced: *α*. By oxidation of paralactic acid, $CH^2OH—CH^2—COOH$ (p. 771).—*β*. By oxidation of allylene, C^3H^4, with an alkaline solution of permanganic acid (Berthelot, *Jahresb.* 1867, p. 335).—*γ*. By boiling barbituric acid with potash (Baeyer, v. 962; see also Heintzel, *Ann. Ch. Pharm.* cxxxix. 129; *Jahresb.* 1866, p. 397):

$$C^4H^4N^2O^3 + 3H^2O = CO^2 + 2NH^3 + C^3H^4O^4.$$

Finkelstein (*Ann. Ch. Pharm.* cxxxiii. 338) prepares malonic acid by boiling crude cyanacetic acid with excess of strong potash-ley; neutralising the diluted solution with acetic acid; precipitating with lead acetate; decomposing the lead malonate with dilute sulphuric acid; evaporating the filtrate; and recrystallising the crystalline residue from a larger quantity of ether, in order to free it from an adhering syrupy substance. The ethereal solution when left to evaporate yields malonic acid in slightly coloured laminæ, or in large prisms having a laminated structure. When recrystallised from water, it is obtained, according to Knop's measurements, in triclinic combinations of $\infty P'_{,} . \infty{,}P . m{,}P'\infty . {,}P$, with two faces bevelling the acute prismatic edges. Cleavage distinct parallel to ${,}P$. Angles $\infty P : \infty P = 113°$ and 67°; $oP : \infty P'_{,} = 110°$; $oP : \infty{,}'P = 86° 30'$; $oP : {,}P = 115° 30'$.[*] Malonic acid is therefore not isomorphous with succinic acid (which crystallises in the rhombic system). It forms acid and neutral salts, all of which, except those of the alkali-metals, are but sparingly soluble; in free malonic acid, acetic acid, or nitric acid they dissolve more readily. The following have been examined:

Potassium salt (acid)	$C^3H^3KO^4 + \frac{1}{2}H^2O$,	colourless prisms.
Sodium salt „	$C^3H^3NaO^4 + \frac{1}{2}H^2O$,	well-defined crystals.
Barium salt *a* .	$C^3H^2BaO^4$,	white precipitate.
Barium salt *b* .	$C^3H^2BaO^4 + H^2O$,	white needles.
Calcium salt . .	$C^3H^2CaO^4 + 1\frac{3}{4}H^2O$,	tufts of needles.

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[*] On account of imperfect reflection, these angular measurements are only approximate.

Magnesium salt	*a*	$C^3H^2MgO^4 + 2H^2O$	crystalline powder.
	b	$C^3H^2MgO^4 + \frac{1}{2}H^2O$	
	c	$C^3H^2MgO^4 + H^2O$	
Manganous salt		$C^3H^2MnO^4 + 2H^2O$,	pale red prisms.
Cobalt salt		$C^3H^2CoO^4 + 2H^2O$,	brown-red powder.
Nickel salt		$C^3H^2NiO^4 + 2H^2O$,	blue-green powder.
Zinc salt		$C^3H^2ZnO^4 + \frac{5}{2}H^2O$,	small crystals.
Cadmium salt		$C^3H^2CdO^4$,	amorphous, deliquescent.
Cupric salt	*a*	$C^3H^2CuO^4 + 3\frac{3}{4}H^2O$,	blue crystals.
	b	$C^3H^2CuO^4.CuO$,	blue-green precipitate.
Lead salt		$C^3H^2PbO^4$,	crystalline powder.
Silver salt		$C^3H^2Ag^2O^4$,	crystalline powder.
Ethylic ether		$C^3H^2(C^2H^5)^2O^4$,	oil boiling at 195°.

The neutral potassium salt and the acid ammonium salt are deliquescent, partially crystalline masses. The barium salt *b* crystallises from the solution of the salt *a* in a large quantity of hot water, and does not give off its water of crystallisation at 150°. The calcium salt gives off ¾ mol. water at 100°. The magnesium salt *a* gives off ½ mol. water at 110°; the salt *b*, which separates from more dilute solutions, gives off all its water at that temperature. The manganese and cobalt salts become anhydrous at 150°; the nickel salt at 170°; the copper salt *a* gives off 2¾ mol. water at 100° (Filkenstein).

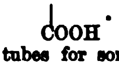
Oxymalonic acid, $C^3H^4O^5$, is formed in small quantity, together with oxalic, acetic, and formic acids, and Reichardt's gum (ii. 955), by oxidising glucose with cupric oxide in alkaline solution. It crystallises in very deliquescent prisms, and forms barium and calcium salts having the composition $C^3H^2M''O^5$ (Claus, *Zeitschr. f. Chem.* [2] v. 152).

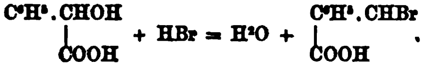
MALTIN. A nitrogenous ferment existing, according to Dubrunfaut, in malt (*Compt. rend.* lxvi. 274; *Zeitschr. f. Chem.* [2] iv. 351), and much more active than diastase. It is precipitated from extract of malt by addition of 2 mol. alcohol of 90 p. c.; and if the addition of alcohol to the solution be continued as long as any precipitate is thereby produced, a substance is obtained, not flocculent like maltin, but syrupy, perfectly soluble in water, and having much less fermentative power than maltin, and containing only a small proportion of nitrogen. As continued treatment with alcohol is recommended by Page and Persoz for the purification of diastase, Dubrunfaut is of opinion that this substance is merely a product of the decomposition of maltin, and that the latter is the really active principle of malt. He further states that maltin is present in all cereal grains, and in the water of rivers and brooks; the well-water of Paris does not however contain it.

MAMANITE. A triple sulphate, $K^2SO^4.2MgSO^4.3CaSO^4 + 3H^2O$, occurring as a deposit on the carnallite of Maman in Persia (Göbel, *Jahresb.* 1865, p. 900).

MANDELAMIDE. See the next article.

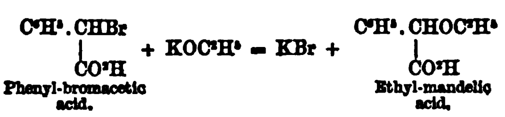
MANDELIC ACID. $C^8H^8O^3$. *Formobenzoic acid* (iii. 799).—This acid has the constitution of phenyl-glycollic acid, $C^6H^5.C^2H^3O^3$ or $\begin{array}{l}C^6H^5.CHOH\\ \vert\\ COOH\end{array}$. When dissolved in fuming hydrobromic acid, and left in sealed tubes for some weeks at ordinary temperatures, or for a few hours at 120°–130°, it is converted into phenyl-bromacetic or α-bromotoluic acid:





$$\begin{array}{l}C^6H^5.CHOH\\ \vert\\ COOH\end{array} + HBr = H^2O + \begin{array}{l}C^6H^5.CHBr\\ \vert\\ COOH\end{array}.$$

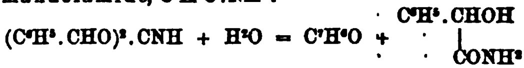
The last acid, heated in concentrated alcoholic solution with alcoholic potash, gives up bromine, and is converted into phenyl-ethyl-glycollic or ethyl-mandelic acid:



$$\underset{\text{Phenyl-bromacetic acid.}}{\begin{array}{l}C^6H^5.CHBr\\ \vert\\ CO^2H\end{array}} + KOC^2H^5 = KBr + \underset{\text{Ethyl-mandelic acid.}}{\begin{array}{l}C^6H^5.CHOC^2H^5\\ \vert\\ CO^2H\end{array}}$$

On neutralising the product with hydrochloric acid, filtering from potassium bromide, and evaporating, ethyl-mandelic acid is obtained as a yellow oil, which when purified by conversion into a barium salt, separation by sulphuric acid, and evaporation, forms a viscid mass resembling bird-lime. Its salts are likewise amorphous (Glaser a. Radziszewski, *Zeitschr. f. Chem.* [2] iv. 140).

When the compound of benzoic aldehyde and hydrogen cyanide, $(C^7H^6O)^2.CNH$ (produced by treating bitter almond oil with hydrocyanic and hydrochloric acids, p. 329), is heated to 180° with water or alcohol, it is completely resolved into benzoic aldehyde and mandelamide, $C^8H^7O.NH^2$:



$$(C^6H^5.CHO)^2.CNH + H^2O = C^7H^6O + \begin{array}{l} C^6H^5.CHOH \\ | \\ CONH^2 \end{array}$$

Hydrocyanide of Benzoic aldehyde. Benzoic aldehyde. Mandelamide.

Mandelamide crystallises in rhombic or hexagonal tables, soluble in water and in boiling alcohol, slightly soluble in ether, melting at 131°, and not wholly volatile without decomposition. Heated with baryta-water to 180°, it is converted into barium mandelate, $(C^8H^7O^3)^2Ba$, which crystallises in small rhombic tables soluble in 6·17 pts. of boiling water, and in 12·3 pts. water at 23° (Zinin, *Zeitschr. f. Chem.* [2] iv. 709).

MANGANESE. This metal is precipitated by sodium-amalgam from acidulated solutions as an amalgam, which when distilled in a stream of hydrogen leaves the metal in form of a pulverulent sponge (*Bull. Soc. Chim.* [2] vi. 93).

Detection and Estimation.—For the detection of manganese in solid bodies, C. D. Braun (*Zeitschr. anal. Chem.* vi. 73) heats the substance in the oxidising flame for two or three minutes in a bead of sodium pyrophosphate, and moistens the bead, after cooling, with nitric acid, whereupon the presence of manganese is indicated by the reddish-violet colour of manganic pyrophosphate, either immediately, or after renewed heating in the oxidising flame. The formation of manganic pyrophosphate may also be made available for the detection of manganese in solution. A moderately concentrated solution of sodium pyrophosphate is mixed with the liquid to be tested for manganese, till the resulting precipitate no longer dissolves, after which a small quantity of lead dioxide is added, and the liquid is boiled and filtered. If manganese is present, the brown filtrate will assume a violet-red to violet-brown colour when mixed with a little hydrochloric acid and gently heated. To detect manganese in vegetable substances, they are gradually added to a melting mixture of 5 pts. nitre and 1 pt. sodium pyrophosphate. The blue-green mass repeatedly evaporated with nitric acid, and finally heated to fusion, assumes a lilac colour (Braun).

According to W. Gibbs (*Sill. Am. J.* [2] xliv. 216), manganese may be estimated, like magnesium, as *ammonio-manganous phosphate*. The manganous solution is mixed with a considerable excess of sodium phosphate; the white gelatinous precipitate is dissolved in hydrochloric acid; the liquid then heated to boiling, and ammonia added in excess. The ammonio-manganous phosphate, which separates in pale rose-coloured nacreous scales, is collected on a filter after a quarter of an hour, washed with hot water, and ignited. If it acquires a darker red colour during washing, it must be redissolved in hydrochloric acid, and precipitated at the boiling heat by ammonia, with addition of sodium phosphate.

On the precipitation and estimation of manganese by *ammonium sulphide*, see Classen (*Zeitschr. anal. Chem.* 1869, p. 416; *Zeitschr. f. Chem.* [2] vi. 285).

For the estimation of manganese in iron and iron ores, the following method is given by Eggertz (*Zeitschr. f. Chem.* [2] iv. 506; *Jahresb.* 1868, p. 872). The iron having been dissolved in hydrochloric acid, with addition of a little nitric acid, the solution is evaporated to dryness to separate silica; the dry mass is boiled with chlorine-water till no more red powder is visible; the solution is diluted with water and filtered; and the separated silica, if still red, is treated with strong hydrochloric acid. The acid solution is then nearly neutralised with sodium carbonate, and boiled with sodium acetate to precipitate ferric oxide and alumina, the precipitate being redissolved and again thrown down with sodium acetate, to separate any manganese that may have been precipitated with it in the first instance. The manganese solution is then concentrated and mixed with bromine, till it becomes yellow, whereby the whole of the manganese is precipitated as hydrated dioxide. The liquid is heated on the water-bath to expel dissolved bromine, then filtered, and the precipitate is washed with weak hydrochloric acid (1 p. c.), to remove alkali more quickly. The precipitate dried at 100° consists of $3MnO^2.H^2O$, containing 59·18 p. c. manganese; by heating it is converted into $MnO.MnO^2$, containing 69·62 manganese.

Iron ores are pulverised and fused with an alkaline carbonate, and the fused mass is treated as above.

Manganese may be separated from the *alkaline earth-metals* by mixing the warm hydrochloric acid solution with caustic soda or sodium carbonate till a permanent precipitate is formed, dissolving this precipitate in the smallest possible quantity of hydrochloric acid, adding a quantity of crystallised sodium acetate nearly equivalent to the hydrochloric acid, and precipitating the manganese at the boiling heat as dioxide by means of sodium hypochlorite, added in such quantity as to leave the liquid slightly acid (E. Reichardt, *Zeitschr. anal. Chem.* v. 60). Rube (*ibid.* iv. 241) boils the nearly neutralised solution for two hours with excess of recently precipitated mercuric oxide. The whole of the manganese is then thrown down as dioxide, together with ferric oxide and alumina, while calcium and magnesium remain in solution.

On the separation of manganese from *cobalt*, *nickel*, and *zinc*, see Gibbs (*Sill. Am. J.* [2] xxxix. 58; *Jahresb.* 1865, p. 712). Manganese salts are easily purified from *cobalt*—which occurs in many varieties of the native dioxide—by passing hydrogen sulphide through the solution of the chloride or sulphate, the liquid being kept neutral by suspending manganese carbonate in it. The cobalt is then wholly precipitated as sulphide (Muck, *Zeitschr. f. Chem.* [2] v. 626).

The precipitation of manganese by *ammonium sulphide* is often prevented by the presence of organic ammonium salts. When a solution of manganous chloride is mixed with a large quantity of oxalic acid, then with excess of ammonia and a little ammonium sulphide, no manganese sulphide is precipitated, but needles of manganous oxalate separate after a while. A solution of manganous chloride, to which chloride, oxalate, and sulphide of ammonium are added in succession, yields after a short time a mixed precipitate of manganous sulphide and oxalate. When a solution of manganous oxalate in dilute hydrochloric acid is treated successively with oxalic acid, ammonia, and ammonium sulphide, no precipitate is formed, but crystals (probably of a double salt) separate after some time. When tartaric or citric acid is dissolved by warming in a solution of manganous chloride, and ammonia and ammonium sulphide are then added, no precipitate is formed even after 24 hours. The other metals of the same group, cobalt, nickel, zinc, &c., are precipitated under similar circumstances by ammonium sulphide, either immediately or after some time (How, *Chem. News*, xix. 137).

Volumetric Estimation.—1. When a manganous solution mixed with ferric chloride is treated with excess of a strongly alkaline solution of *potassium ferricyanide*, manganous dioxide (mixed with ferric oxide) is precipitated, while potassium ferrocyanide remains in solution:

$$K^6Fe^2Cy^{12} + 2KHO + MnO = MnO^2 + H^2O + 2K^4FeCy^6.$$

To apply this reaction to the volumetric estimation of manganese, the acid manganous solution is mixed with ferric chloride (1 mol. MnO to 1 mol. Fe^2O^3), and the mixture is added to a solution of the ferricyanide made strongly alkaline with caustic soda. The solution when quite cold is filtered; the brown-black precipitate is washed; the filtrate is concentrated to a definite volume, and acidulated; and the quantity of ferrocyanide in it is determined by titration with potassium permanganate (Lenssen, *J. pr. Chem.* lxxx. 408). According to Fresenius (*Zeitschr. anal. Chem.* iii. 209), this method is especially useful when a considerable number of determinations have to be made, and the quantity of manganese present is not very small.

2. When a solution of a manganous salt (containing all other metals in their highest forms of oxidation) is mixed with *potassium permanganate*, the latter is decolorised, and a violet-brown precipitate of hydrated dioxide, $MnO^2.H^2O$, is formed, insoluble in dilute inorganic acids. The reaction is:

$$3MnCl^2 + 2H^2O + K^2Mn^2O^8 = 2KCl + 4HCl + 5MnO^2,$$

1 mol. of permanganate used corresponding to 5 at. manganese in the solution. A gram or two of the manganese-compound under examination is dissolved in boiling nitromuriatic acid; the solution nearly neutralised with an alkali is made up to a litre with boiling water, and a titrated solution of permanganate is poured into it (the temperature of the liquid being kept up to 80°) till the supernatant liquid retains its colour even after stirring. The permanganate solution is titrated with pure manganous sulphate, so that 30 c. c. of it shall correspond to about 1 grm. of metallic manganese (A. Guyard, *Bull. Soc. Chim.* [2] vi. 89).

The separation of manganese from the metals of the alkalis and alkaline earths, and from nickel, cobalt, and uranium, may also be effected by means of potassium permanganate in the manner above described, the slight excess of the latter being decomposed by ammonia. If a non-titrated solution of permanganate is used, the precipitate must be ignited, and three-fifths of its weight reckoned as manganese (Guyard).

According to Habich (*Zeitschr. anal. Chem.* iii. 474), Guyard's volumetric acid gives exact results when applied to neutral solutions, but not when free sulphuric or hydrochloric acid is present. The presence of ferric or chromic oxide likewise interferes with the correctness of the result.

For Mittenzwey's method of estimating manganese and other substances by oxidation in presence of an alkali, see ANALYSIS, VOLUMETRIC (p. 155).

On the valuation of commercial manganese, see Teschemacher and Denham Smith (*Zeitschr. anal. Chem.* 1869, 314, 509; *Zeitschr. f. Chem.* [2] vi. 287).

Compounds of Manganese.

Chlorides. According to Nicklès (*Ann. Ch. Phys.* [4] v. 161; *Jahresb.* 1865, p. 225), a chloride, $MnCl^4$, analogous to the dioxide, is produced by passing hydrochloric acid gas into a well-cooled mixture of the dioxide with ether. A solution is then obtained of a fine green colour, very unstable, and easily decomposed by reducing agents. It appears to contain ether, water, and the tetrachloride in variable proportions; in one instance its analysis gave results agreeing with the formula $MnCl^4.12(C^2H^5)^2O.2H^2O$. Green unstable solutions are likewise obtained with manganese dioxide, ether, and hydrobromic or hydriodic acid; also when the sesquioxide of manganese is used instead of the dioxide.

Fluorides. The *tetrafluoride*, MnF^4, is produced by treating the ethereal solution of the tetrachloride with aqueous hydrofluoric acid, the colour changing from green to brown; also by treating the dioxide with aqueous hydrofluoric acid. It does not appear to have been obtained pure. It dissolves in alcohol, and, in absence of water, also in ether. The aqueous solution acts as an oxidising agent, and in the dilute state decomposes easily, especially in presence of alkalis or alkaline chlorides, depositing the hydrated dioxide. With potassium fluoride it yields a rose-coloured precipitate which when dried at 100° has the composition $2KF.MnF^4$; with ammonium fluoride a similar but more soluble precipitate; the still more soluble sodium double salt is precipitated only on addition of alcohol. These double fluorides dissolve with violet colour in concentrated aqueous phosphoric acid. In dilute aqueous solution they decompose as easily as the free tetrafluoride of manganese, but become more permanent in presence of an excess of alkaline fluoride. They are fusible, acquiring a transient blue colour while melted; and are decomposed by prolonged fusion, with formation of a basic double fluoride, *e.g.* $8KF.MnF^4$. A similar basic salt is formed by fusing manganese dioxide with potassium fluoride. A few double fluorides of manganese and other heavy metals have been obtained by double decomposition, and similar but very unstable compounds containing organic bases by saturating the aqueous solution of manganese tetrafluoride with the corresponding bases. When manganese tetrachloride is added by drops to a boiling solution of potassium or ammonium fluoride, a rose-coloured powder separates, consisting, according to Nicklès, of an oxyfluoride, $MnOF^2$, and forming with potassium fluoride the double salt $2KF.MnOF^2$. The tetrafluoride and oxyfluoride of manganese are obtained in ethereal solution by treating their potassium salts with anhydrous ether saturated with silicon fluoride. The solutions are brown and give up manganese tetrafluoride or oxyfluoride to water when agitated therewith. *Manganese trifluoride*, Mn^2F^6 (ii. 808), also yields double fluorides and oxyfluorides when similarly treated with solutions of alkaline fluorides, *e.g.* the salt $4KF.Mn^2F^4O$. A potassium salt belonging to one of these groups is formed, with elimination of ozone, by the action of aqueous hydrofluoric acid on potassium permanganate (Nicklès, *Bull. Soc. Chim.* [2] viii. 408).

In treating manganese dioxide with hydrofluoric acid for the preparation of the tetrafluoride as above, there are sometimes obtained, especially when heat is applied (perhaps also only when the manganese dioxide is mixed with manganoso-manganic oxide, Mn^3O^4), brown crusts of *manganoso-manganic fluoride*, $Mn^3F^8 + 10H^2O$ or $MnF^2.Mn^2F^6 + 10H^2O$. This compound dissolves with brown colour in a small quantity of water, but is decomposed by a large quantity, with separation of brown oxide, and more completely by alkaline carbonates. It forms a rose-coloured precipitate both with potassium fluoride and with manganic fluoride. Its solution takes up large quantities of metallic silver, being converted at the same time into colourless manganous fluoride. Potassium fluoride added to this solution throws down a precipitate of variable composition (containing about 1 p. c. manganese and 50 p. c. silver); lead precipitates the silver, but is not itself dissolved (Nicklès, *Bull. Soc. Chim.* [2] xi. 411).

Oxides. Analyses of manganite and pyrolusite from Nova Scotia are given by How (*Phil. Mag.* [4] xxxi. 165; *Jahresb.* 1866, 923). E. Schmid (*Pogg. Ann.* cxxvi. 151; *Jahresb.* 1865, 878) has analysed psilomelane from Oehrenstock, from Elgersburg, and from Nadabula in Hungary. For the mineral from Elgersburg, he deduces the formula $(BaO ; MnO).4MnO^2 + 6aq$.

Respecting the regeneration of manganese dioxide from waste chlorine-liquors, see CHLORINE (p. 435).

Manganates.—A pigment called *Cassel green* is prepared by igniting 14 pts. manganese dioxide with 80 pts. nitrate and 6 pts. sulphate of barium, or 24 pts. manganous oxide with 40 pts. nitrate and 30 pts. sulphate of barium. The green fritted mass is triturated with water and mixed in the moist state with gum or dextrin (Schad, *Bull. Soc. Chim.* [2] v. 477; see also Rosenstiehl, *Dingl. pol. J.* clxxvii. 409).

Permanganates.—To avoid the loss arising in the preparation of potassium permanganate from the separation of hydrated dioxide, Städeler (*J. pr. Chem.* ciii. 107) effects the conversion of the manganate into permanganate by means of chlorine gas:

$$2MnK^2O^4 + Cl^2 = 2KCl + Mn^2K^2O^8.$$

The crude pulverised manganate is left to soften for some hours in contact with water; an equal quantity of water is then added; and chlorine is passed into the liquid till it turns red. The solution is then diluted with four times its bulk of water; and after clarification by subsidence, or filtration through pounded glass, is evaporated to one-fifth of its volume. The greater part of the permanganate then separates out, and may be purified by recrystallisation. The product amounts on the average to 90 p. c. of the manganese dioxide used.

Potassium permanganate is reduced by hydrogen dioxide, with formation of potassium hydrate, and precipitation of hydrated sesquioxide and dioxide of manganese, the proportion of these oxides in the precipitate varying according as the solution of hydrogen dioxide is neutral or acid (Weltzien, *Compt. rend.* lxii. 642; *Ann. Ch. Pharm.* cxxxviii. 140. Swionkowski, *ibid.* cxli. 205; *Jahresb.* 1867, p. 248).

According to Linder (*Zeitschr. f. Chem.* [2] v. 442), soluble *iodides* are converted by dilute potassium permanganate into iodates; *bromides* in acid solution react like iodides; but in neutral or alkaline solution they do not reduce the permanganate; *chlorides* do not reduce it either in alkaline or in acid solution.

A solution of potassium permanganate is easily decomposed at ordinary temperatures by metallic *mercury*, with formation of mercurous oxide, manganic hydrate, and potassium hydrate; more quickly at the boiling heat, with immediate formation of mercuric oxide. *Silver* appears also to be attacked by the permanganate; on zinc and copper it does not act (W. B. Giles, *Chem. News*, xv. 204). *Thallium* is oxidised by the permanganate solution at ordinary temperatures; *magnesium* and *aluminium* only at the boiling heat, and even then but slowly (Crookes, *ibid.*).

Cane-sugar, *milk-sugar*, *starch*, and *gum* are completely oxidised by potassium permanganate in acid solution, to carbonic acid and water; equal quantities of starch and gum reduce nearly equal quantities of the permanganate. *Tartaric acid* and *naphthalene* are likewise oxidised (Langbein, *Zeitschr. f. Chem.* [2] v. 350).

Ammonium salts heated to 150° in sealed tubes, with about 40 times their weight of potassium permanganate, and a 50 p. c. solution of potash, give off no nitrogen, and yield only traces of ammonia. Acetamide reacts in a similar manner. The nitrogen must therefore be converted, under these circumstances, into nitric or nitrous acid, as formerly found by Schönbein, Cloez, and Guignet (*Jahresb.* 1858, p. 171), also by Wöhler (*ibid.* 1865, p. 150). *Urea* heated in sealed tubes to 160°–200°, with a strongly alkaline solution of permanganate, gives off part of its nitrogen in the free state, while nearly all the rest is converted into nitric acid, with only a trace of ammonia; but when the urea is distilled for some time in an open vessel with dilute potash containing permanganate, 22 p. c. of the nitrogen appears as ammonia (Wanklyn a. Gamgee, *Chem. Soc. J.* [2] vi. 25). *Asparagine*, *piperine*, *piperidine*, *amylamine*, *diamylamine*, *hippuric acid*, *narcotine*, and *diphenyl-tartramide*, heated with a strongly alkaline solution of potassium permanganate, give off nearly the whole of their nitrogen as ammonia; *morphine*, *codeine*, *papaverine*, *strychnine*, *iodomethyl-strychnine*, *brucine*, *quinine*, *cinchonine*, *nicotine*, *toluidine*, and *rosaniline*, only about half; *creatine* about a third; *caffeine* about a fourth; *uric acid* about a fifth; *gelatin* 12·7 p. c.; *albumin* about 10 p. c.; *casein* 6·5 p. c. *Picric acid* thus treated yields no ammonia (Wanklyn a. Chapman, *Chem. Soc. J.* [2] vi. 161). On the action of permanganate on quinine, see that base.

Sulphides. Manganous sulphide is formed, together with a polysulphide of potassium, by heating potassium manganate in vapour of carbon bisulphide:

$$K^2MnO^4 + 2CS^2 = MnS + K^2S^3 + 2CO^2.$$

A similar product is obtained with barium manganate (W. Müller, *Pogg. Ann.* cxxvii. 404).

By heating the amorphous sulphide in a stream of hydrogen sulphide, it is obtained in yellow-green hexagonal prisms. At the same time very small shining laminar crystals of unknown composition are formed, grouped in squares or crosses (Sidot, *Compt. rend.* lxvi. 1257).

On the behaviour of flesh-coloured manganese sulphide with various reagents, see Muck (*Zeitschr. f. Chem.* [2] vi. 6).

MANNITE. $C^6H^{14}O^6 = \left.\begin{matrix}(C^6H^8)^{vi}\\ H^6\end{matrix}\right\}O^6$.—Respecting its constitution, see ALCOHOLS (p. 72).

The compounds of mannite with the alkaline earths which Ubaldini obtained by triturating mannite with hydrate of barium, calcium, &c., and water, and precipitating with alcohol (*Gmelin's Handbook*, xv. 365), have been further examined by Hirzel (*Ann. Ch. Pharm.* cxxxi. 50; *Jahresb.* 1864, p. 581), who finds for the barium compound the formula $2C^6H^{14}O^6.BaO$; for the calcium compound, $4C^6H^{14}O^6.3CaO$; and for the strontium compound, $4C^6H^{14}O^6.SrO$.

Silver nitrate, mercurous nitrate, auric chloride, and mercuric chloride are not reduced by mannite even at the boiling heat; silver acetate or silver oxide heated with mannite, or left in contact with it at ordinary temperatures, yields a speculum of silver. Hydrogen dioxide converts mannite into an acid substance, which reduces an alkaline cupric solution.

Acetyl-mannites.—Mannite heated with acetic anhydride containing 10·15 p. c. glacial acetic acid gradually dissolves, the liquid solidifying on cooling to a crystalline mass surrounded by a syrupy liquid. On filtering this mass in an imperfect vacuum through asbestos, and washing the residue with absolute alcohol, a white very light mass is obtained, having the composition of acetyl-dimannitan, $C^{12}H^{22}(C^2H^3O)O^{10}$. It has a bitter taste, is very slightly lævogyrate, nearly insoluble in boiling alcohol, insoluble in ether, very soluble in water and in acetic acid; melts at 120°; yields mannitan by saponification. By prolonged action of the acetic anhydride, a thick syrup is obtained, from which water separates white crystalline grains; and the mother-liquor yields, when evaporated over the water-bath, a colourless, transparent, nearly solid, very sweet syrup, having a strong lævogyrate power, $[\alpha] = -22·6°$. The white crystalline precipitate exhibits, after recrystallisation from alcohol, the composition of hexacetyl-mannite, $C^6H^8(C^2H^3O)^6O^6$. It is optically inactive, melts at about 100° and resolidifies in the crystalline form on cooling. The syrupy compound above-mentioned appears to have the composition $C^6H^8(C^2H^3O)^2O^4$, and is probably identical with Berthelot's so-called diacetyl-mannitan (E. Grange, *Compt. rend.* lxviii. 1326; *Zeitschr. f. Chem.* v. 448).

MARACAIBO BALSAM. }
MARANHAN BALSAM. } See COPAIBA.

MARCELLINE. This mineral, from St. Marcel in Piedmont, has, according to G. Rose (*Pogg. Ann.* cxxi. 318), the composition $MnO.MnO^2.SiO^2$; sp. gr. 4·752.

MARCYLITE. This mineral, from the Red River in the neighbourhood of Mount Wichita, has, according to S. W. Tyler (*Sill. Am. J.* [2] xli. 209), essentially the composition $CuS.CuO + H^2O$, the ferrous sulphide and gypsum contained in it being regarded as adventitious.

MARGARYLENE. $C^{11}H^{22}$.—One of the hydrocarbons obtained by the dry distillation of Menhaden oil soap (p. 814). Boils at 193°–196°.

MAUVANILINE. $C^{19}H^{17}N^3 = \left.\begin{matrix}(\overset{\prime\prime}{C^6}H^4)^2\\ (C^7H^6)''\\ H^3\end{matrix}\right\}N^3$ (De Laire, Girard, a. Chapoteaut, *Compt. rend.* lxiv. 416; *Bull. Soc. Chim.* [2] vii. 366; *Jahresb.* 1867, p. 507, 962).—A base produced by the action of dehydrogenising agents on a mixture of aniline and toluidine:

$$2C^6H^7N + C^7H^9N - 6H = C^{19}H^{17}N^3.$$

It may be prepared by heating 100 pts. of commercial aniline (boiling at 183°–188°, and consisting of a mixture of 2 mol. phenylamine and 1 mol. toluidine) with 115 pts. dry arsenic acid. or 164 pts. of a solution containing 70 p. c. arsenic anhydride, to 170° for some hours, in the same way as for the preparation of rosaniline, treating the product with boiling water to dissolve any salts of chrysotoluidine and rosaniline that may have been formed, and decomposing the remaining arsenite and arsenate of mauvaniline with caustic soda. The impure base, after being separated and washed, is dissolved in dilute hydrochloric acid, and the solution is precipitated by sodium chloride, the rest of the chrysotoluidine then remaining dissolved; or the crude base may be treated with ether and benzol to dissolve the mauvaniline and chrysotoluidine, which may then be separated by solution in hydrochloric acid and precipitation with sodium chloride as above. The residue insoluble in dilute acids, and in ether or benzol, consists chiefly of violaniline. All other oxidising agents used for the preparation of rosaniline may also be applied to that of mauvaniline. This base occurs, in fact, in the residues of the industrial preparation of rosaniline, and is perhaps the cause of the violet tint sometimes exhibited by commercial aniline-red.

Mauvaniline forms light brown crystals, which give off their water (½ mol.), with decomposition, above 130°. It is soluble in ether, benzol, and alcohol, very slightly in hot water, insoluble in cold water. Its salts (especially the acetate and hydrochloride) crystallise readily, and exhibit a bronze-green reflex like those of rosaniline. They are somewhat soluble in cold, more easily in hot or acidulated water, and dye silk and wool a fine mallow-red.

Triphenyl-mauvaniline, $C^{19}H^{14}(C^6H^5)^3N^3$, produced by the action of aniline on mauvaniline, is a yellowish-white crystalline mass, insoluble in water, soluble in ether and in alcohol; its salts have a splendid blue colour.

Triethyl-mauvaniline, prepared like the corresponding derivative of rosaniline, is white, crystalline, soluble in alcohol and ether; its salts impart a fine blue-violet colour to silk and wool.

MAUVEINE, the base of mauve or aniline purple (iv. 466), is now regarded by Perkin as consisting of $C^{26}H^{24}N^4$ or $(C^{26}H^{20})^{viii}H^4N^4$ (*Lecture delivered at the Royal Institution*, May 14, 1869).

MECONIC ACID. $C^7H^4O^7$.—This acid suspended in water is converted by sodium-amalgam into hydromeconic acid, $C^7H^{10}O^7$, which when separated from its lead salt by hydrogen sulphide and evaporated, remains as a strongly acid syrup, easily soluble in water, less soluble in alcohol, and precipitated therefrom by ether in deliquescent flocks. It is completely decomposed by heat, but not attacked by bromine or nitric acid. The following hydromeconates have been examined:

Barium salt,	$C^7H^8BaO^7 + 2H^2O$,	amorphous precipitate, soluble in water, insoluble in alcohol.
Lead salt,	$C^7H^8PbO^7 + 1\frac{1}{2}H^2O$,	amorphous precipitate.
Silver salt,	$C^7H^8Ag^2O^7 + \frac{1}{2}H^2O$,	white granular precipitate.

Meconic acid is not further reduced by hydriodic acid, but resolved, as by hydrochloric acid, into carbon dioxide and comenic acid. Hydriodic acid does not act upon hydromeconic acid. Meconic acid forms with *aniline* a beautifully crystallised salt, $C^7H^4O^7.2C^6H^7N$, which is converted by heat into comenate, $C^6H^4O^5.C^6H^7N$ (J. v. Korff, *Ann. Ch. Pharm.* cxxxvii. 191).

MECONIDINE. $C^{21}H^{23}NO^4$ (Hesse, *Ann. Ch. Pharm.* cliii. 47; *Chem. Centr.* 1870, 167).—A base contained, together with others, in the aqueous extract of opium, and remaining in solution after the codamine (p. 480) has crystallised out. When the crystals of the latter no longer appear to increase, the mother-liquor is decanted, the bases contained in it are combined with dilute acetic acid, and the acid solution is saturated with common salt, whereby hydrochloride of meconidine is thrown down, whilst the salts of a fourth base (x) remain for the most part in solution. The meconidine precipitate, which is of resinous consistence, is redissolved in cold water, with addition of a little acetic acid, and again precipitated with common salt, which operation is once more repeated. Lastly the salt thus purified is dissolved in a small quantity of cold water; the solution is mixed with excess of sodium bicarbonate and agitated with ether; the ethereal solution is filtered through animal charcoal; and the ether is left to evaporate, whereupon the meconidine remains as a yellowish varnish, very easily dried at 90°.

Meconidine forms a brownish-yellow transparent amorphous mass, which when touched splits up into innumerable small laminæ, and may be ground to a yellowish powder. Melts at 58°; not sublimable; burns away completely when heated in the air. It is tasteless; insoluble in water, but very soluble in *alcohol*, *ethre*, *benzol*, *chloroform*, and *acetone*. The alcoholic solution blues reddened litmus, and neutralises sulphuric, hydrochloric, and acetic acids.

Meconidine is easily decomposed by strong *acids*, especially if heated. Its solution in dilute sulphuric acid becomes rose-coloured in a few minutes, purple-red in a few hours; at the boiling heat these changes of colour take place immediately. With acetic acid the change is much slower. Ammonia produces in the purple-red solution a dirty-white, very changeable precipitate. Strong sulphuric acid dissolves meconidine with olive-green colour; strong nitric acid colours it orange-red.

The *salts* of meconidine are very unstable. Their dilute solutions have an intensely bitter taste. From the acetic acid solution the meconidine is precipitated by *potash* or *soda* in white flocks, but is redissolved by excess of the reagent, and may be separated from the alkaline solution, after addition of sal-ammoniac, by ether, chloroform, and other solvents; acids precipitate it from the alkaline solution, but redissolve it when added in excess. *Ammonia* likewise precipitates the base, redissolves it when added in very large excess, but gives it up to ether or chloroform when agitated therewith. *Lime* reacts in a similar manner. The reaction with potash distinguishes meconidine from rhœadine, the salts of which give with potash a permanent crystalline precipitate.

Platinochloride of meconidine, $2(C^{21}H^{23}NO^4).PtCl^4$, is a yellow amorphous precipitate, which soon turns reddish. The *aurochloride* is a dingy yellow amorphous precipitate; the *mercurochloride* is a white amorphous precipitate, which in contact with hydrochloric acid soon acquires a rose colour.

MELACONITE. Native cupric oxide found at Copper Harbour, Lake Superior, in monoclinic crystals (Maskelyne, *Br. Assoc. Reports*, 35; *Notices and Abstracts*, 33; *Jahresb.* 1867, p. 979).

MELAMINE. $C^3H^6N^6$.—Syn. with CYANURAMIDE (ii. 287).

Triethyl-melamine, $C^3H^3(C^2H^5)^3N^6$, is produced by desulphuration of ethyl-sulphocarbamide. (See SULPHOCARBAMIDES.) By prolonged contact with cold hydrochloric acid, or by boiling for a short time with the same acid, it is converted into ammonia and triethyl-ammelide:

$$C^3H^3(C^2H^5)^3N^6 + H^2O = NH^3 + C^3H^2(C^2H^5)^3N^5O.$$

The platinochloride of triethyl-ammelide, $2[C^3H^2(C^2H^5)^3N^5O.HCl].PtCl^4$, crystallises in beautiful four-sided prisms, very easily soluble in water, less soluble in alcohol, not decomposed at 100° (Hofmann, *Zeitschr. f. Chem.* [2] vi. 158).

MELAPHYRE. Analysis of this rock from Norheim near Kreuznach and Kokos in the Dobrudscha, are given by Laspeyres (*Jahresb.* 1865, p. 922) and Sommaruga (*ibid.* 1866, p. 978).

MELILOTIC ACID. Syn. with HYDROCOUMARIC ACID (p. 715).

MELISSIN. $C^{31}H^{64}O$.—This alcohol occurs in Canaüba wax (p. 391).

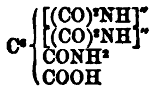
MELLITIC ACID. $C^{12}H^6O^{12}$ (Baeyer, *Ann. Ch. Pharm. Suppl.* vii. 1; Preliminary Notice, *Berl. Akad. Ber.* 1866, p. 77; *Ann. Ch. Pharm.* cxli. 271; further, *Deut. chem. Ges. Ber.* 1871, 273; *Chem. Soc. J.* [2] ix. 372).—This acid, formerly represented by the formula $C^4H^2O^4$, and regarded as bibasic, has been shown by Baeyer's investigations to be sexbasic, and to have the constitution of benzene-hexcarbonic acid, $C^6(CO^2H)^6$—that is, to consist of benzene in which all the six carbon-atoms are replaced by carboxyl.

The composition of the salts and ethers of mellitic acid, according to the six-carbon formula, may be illustrated by the following examples:

Neutral.	Acid.
$C^{12}O^{12}(NH^4)^6$	$C^{12}O^{12}H^4(NH^4)^2$
$C^{12}O^{12}(CH^3)^6$	$C^{12}O^{12}H^3K^3$
$C^{12}O^{12}(C^2H^5)^6$	$C^{12}O^{12}H^4(C^2H^5)^2$
$C^{12}O^{12}Ba''^3$	$C^{12}O^{12}H^2Cu''^2$
$C^{12}H^{12}(Al^2)^{vi}$	

Mellitic chloride, obtained by H. Müller (iii. 874) by the action of phosphorus pentachloride on mellitic acid, has the composition $C^6(COCl)^6$. Müller described it as non-volatile, but Baeyer finds that, on distilling the product in a stream of air, the mellitic chloride passes over (after the $POCl^3$ and excess of PCl^5) as a colourless oil, which solidifies to a crystalline mass on cooling. It dissolves easily in pure ether, is insoluble in water, and is slowly converted by boiling therewith into mellitic acid.

Mellitic acid is capable of yielding a large number of amidogen derivatives. Between mellitamide, $C^6(CONH^2)^6$, and mellitic acid, $C^6(COOH)^6$, there may exist five amidated acids, admitting of several isomeric modifications. Mellitamide by giving up ammonia is converted into a tri-imide, viz. **paramide**, $C^6\left(\begin{matrix}CO\\CO\end{matrix}\!>\!NH\right)^3$. Between this compound, the amide, and the acid, there may further exist numerous intermediate compounds, two of which are known, viz. **paramic acid** and **euchroic acid** (ii. 601), which are probably related as follows. When paramide is dissolved in ammonia, and the solution immediately treated with hydrochloric acid, it deposits **paramic acid**:



$$C^6\left\{\begin{matrix}[(CO)^2NH]''\\ [(CO)^2NH]''\\ CONH^2\\ COOH\end{matrix}\right. ,$$

one of the bivalent imidogen groups, $(CO)^2NH$, of the paramide being converted by assumption of water into the two univalent groups $CONH^2$ and $COOH$. If now the amidogen group $CONH^2$ takes up H^2O and gives off ammonia, a second acid group $COOH$ will be formed, and the result will be **euchroic acid**, $C^6\left\{\begin{matrix}[(CO)^2NH]^2\\ (COOH)^2\end{matrix}\right.$.

Acids derived from Mellitic Acid.

Mellitic acid heated with lime is completely resolved into carbon dioxide and benzene:

$$C^6(CO^2H)^6 = 6CO^2 + C^6H^6.$$

It is in fact the last term of the series of aromatic acids derived from benzene by substitution of CO^2H for H—the first term being benzoic acid—all of which are resolved in like manner by distillation with lime into carbon dioxide and benzene, The formulæ of these acids are as follows:

$$\begin{array}{l|l} C^6H^5(CO^2H) & C^6H^2(CO^2H)^4 \\ C^6H^4(CO^2H)^2 & C^6H(CO^2H)^5 \\ C^6H^3(CO^2H)^3 & C^6(CO^2H)^6. \end{array}$$

The first and fifth, and mellitic acid itself, are not susceptible of isomeric modifications; but the second, third, and fourth, each admit of three modifications, accordingly as the carboxyl occupies, in the second, the places (1, 2), (1, 3), or (1, 4); in the third the places (1, 2, 3), (1, 2, 4), or (1, 2, 5); and in the fourth the places (1, 2, 3, 4), (1, 2, 3, 5), or (1, 2, 4, 5): in all twelve different acids. (See AROMATIC SERIES, p. 197.)

One modification of the fourth acid of the series (pyromellitic acid, $C^{10}H^6O^8$) is produced by distilling mellitic acid alone at a moderate heat; and by heating mellitic acid to duly regulated temperatures, either alone or with bases, it is possible that the other acids of the series might also be obtained.

All the twelve acids above enumerated are known, except the fifth. They are produced by the following series of processes:

Mellitic acid treated with sodium-amalgam takes up 6 atoms of hydrogen—one for each atom of carboxyl—and is converted into **hydromellitic acid**, $C^6H^6(CO^2H)^6$. This acid heated with strong sulphuric acid loses 6 atoms of hydrogen, and at the same time 2 mol. carbon dioxide, and is converted into two isomeric quadribasic acids, called **prehnitic** and **mellophanic acids**:

$$C^6H^6(CO^2H)^6 = H^6 + 2CO^2 + C^6H^2(CO^2H)^4.$$

In like manner, prehnitic acid treated with sodium-amalgam, takes up an atom of hydrogen for each of its atoms of carboxyl, forming **hydroprehnitic acid**, $C^6H^6(CO^2H)^4$, and this acid heated with strong sulphuric acid is converted into tribasic trimesic acid:

$$C^6H^6(CO^2H)^4 = H^4 + CO^2 + C^6H^3(CO^2H)^3.$$

This last compound can in like manner take up 3 at. hydrogen, and the resulting acid, $C^6H^6(CO^2H)^3$, heated with sulphuric acid, will yield bibasic **isophthalic acid**, $C^6H^4(CO^2H)^2$; but the latter may be obtained more directly by simply heating hydroprehnitic acid.

Mellophanic acid undergoes similar transformations, resulting in the formation of hemimellitic and phthalic acids.

In the chain of reactions just described, the carboxyls are removed from mellitic acid in a certain order; this however is not the only method of passing from the sexbasic to the monobasic acid. Mellitic acid when heated yields **pyromellitic acid**,

$C^6H^2(CO^2H)^4$; and this acid treated with sodium-amalgam takes up 4H and is converted into hydropyromellitic acid, $C^6H^6(CO^2H)^4$, which when heated with strong sulphuric acid yields trimellitic acid, $C^6H^3(CO^2H)^3$, isomeric with hemimellitic acid; and this again would doubtless take up hydrogen, yielding a product decomposible by sulphuric acid. In the formation of trimellitic acid, isophthalic acid is obtained as a secondary product.

Hydromellitic Acid. $C^{12}H^{12}O^{12} = C^6H^6(CO^2H)^6$.—Mellitic acid is easily hydrogenised by sodium-amalgam, especially in presence of ammonia. The resulting hydromellitic acid may be purified by precipitating the neutralised solution with lead acetate, and decomposing the precipitate with hydrogen sulphide. On evaporating the filtrate, the hydromellitic acid remains as a syrup, which gradually solidifies to indistinct crystals like those of grape-sugar. It is colourless, very hygroscopic, but not actually deliquescent; dissolves very easily in water, forming a strongly acid liquid; also in alcohol, but sparingly in ether. When heated it melts, with loss of water, to a colourless liquid, which decomposes at a higher temperature, giving off carbon dioxide and leaving a large quantity of charcoal.

The hydromellitates of the alkali-metals are easily soluble in water; of those of the earth-metals and heavy metals, some are soluble, others insoluble. Many are precipitated from their solutions by heat, like calcium citrate, and redissolve on cooling; this is the case with the *calcium* and *manganese salts*. The *silver salt* contains $C^{12}O^{12}H^6Ag^6$; the *lead salt* $C^{12}O^{12}H^6Pb^3$. The ethylic ether, $C^{12}O^{12}H^6(C^2H^5)^6$, formed by passing hydrochloric acid gas into the alcoholic solution of the acid, is a viscid oil insoluble in water, and decomposing when heated, giving off gas, and yielding a distillate consisting of a liquid and a solid body. The solid body crystallises in large prisms soluble in alcohol, melting between 128° and 130°, and yielding by analysis numbers intermediate between those required by the formulæ $C^6H^2(CO^2C^2H^5)^4$ and $C^6H^4(CO^2C^2H^5)^2$. The liquid portion of the distillate consists of the ethers of acids richer in hydrogen, one of which, judging from the odour, is hydrobenzoic acid.

Hydromellitic acid heated for some time with *phosphorus pentachloride* and excess of the *oxychloride*, apparently yields hydromellitic chloride. Oxidising agents, *e.g. permanganates* and *nitric acid*, act but slowly on hydromellitic acid; in a mixture of strong nitric and sulphuric acids, it dissolves without apparent alteration. By heating or by prolonged contact with *hydrobromic acid* it is converted into isohydromellitic acid. Heated to 130° in a sealed tube with 6 at. *bromine*, it is partly converted into hydrobromic acid and brominated benzocarbonic acids, and perhaps also yields a small quantity of benzocarbonic acids containing smaller proportions of carboxyl. At the same time the hydrobromic acid converts part of the hydromellitic into isohydromellitic acid.

Respecting the difference of constitution between mellitic and hydromellitic acids, see p. 814.

Isohydromellitic acid, $C^{12}H^{12}O^{12}$, is obtained as above described in tufts of short thick needles, easily soluble in water, but precipitated from the concentrated solution by hydrochloric acid. It crystallises immediately from the aqueous solution in rather large, hard, thick, four-sided prisms, without first becoming syrupy like hydromellitic acid. The crystals are anhydrous, and melt with intumescence when heated, giving off a small quantity of acid water, and leaving a large quantity of charcoal. It is a very stable compound, not being altered by heating to 300° with fuming hydrochloric acid, or by heating with a mixture of sulphuric and fuming nitric acids. It is slowly oxidised by potassium permanganate, rapidly by chromic acid mixture, giving off carbon dioxide and yielding acetic acid, together with a small quantity of trimesic acid.

Isohydromellitic acid yields with *barium acetate* a flocculent precipitate slightly soluble in acetic acid, the solution becoming turbid when heated; with *manganous acetate* no precipitate in the cold, but a flocculent precipitate when heated, which redissolves on cooling; with *silver nitrate* a white granular precipitate easily soluble in ammonia and in nitric acid; with *lead acetate* a flocculent precipitate of the salt $C^{12}O^{12}H^6Pb^3$, nearly insoluble in water, and very slightly soluble in warm dilute acetic acid. *Methylic isohydromellitate* is easily formed by the action of methyl iodide on the silver salt, and crystallises in needles insoluble in water, easily soluble in alcohol, melting at 125°, and often remaining liquid for a long time after evaporation of the alcoholic solution.

Hydromellitic or isohydromellitic acid heated with five times its weight of strong *sulphuric acid* to about the boiling point of the latter, gives off carbonic and sulphurous anhydrides, and yields a brown liquid, which when mixed with a sufficient quantity of water to redissolve the precipitate first formed, then agitated with ether, and freed from ether by distillation, yields a reddish nodular crystalline mass easily soluble in water, excepting a small portion. The soluble substance is isopyromellitic acid; the insoluble, trimesic acid. Their formation is represented by the following equations:

$$\underset{\text{Hydromellitic.}}{C^6H^6(CO^2H)^6} + 3SO^4H^2 = 2CO^2 + 3SO^2 + 6H^2O + \underset{\text{Isopyromellitic.}}{C^6H^2(CO^2H)^4}$$

and

$$\underset{\text{Hydromellitic.}}{C^6H^6(CO^2H)^6} + 3SO^4H^2 = 3CO^2 + 3SO^2 + 6H^2O + \underset{\text{Trimesic.}}{C^6H^3(CO^2H)^3}$$

These two acids are purified by converting them into lead salts, separating with hydrogen sulphide, evaporating to a small bulk, adding a little sulphuric acid, and exhausting with ether. The same mode of purification is applicable to all the corresponding acids to be further described.

Trimesic Acid. $C^9H^6O^6$.—Fittig (*Ann. Ch. Pharm.* cxli. 129; *Jahresb.* 1866, p. 607) obtained this acid by the action of potassium dichromate and sulphuric acid on mesitylenic acid:

$$C^9H^{10}O^2 + 6O = C^9H^6O^6 + 2H^2O.$$

It is moderately soluble in water and ether, easily in alcohol, and crystallises from hot water in hard, thick, colourless prisms, which volatilise at a very high temperature without previous fusion; and sublime in needles. The *barium salt*, $(C^9H^3O^6)^2Ba^3 + 2H^2O$, separates on mixing the slightly ammoniacal solution of the acid with barium chloride, as a crystalline pulp composed of rather large needles; it is but slightly soluble in water, even at the boiling heat, and is easily decomposed by hydrochloric acid, with separation of trimesic acid. The *silver salt*, $C^9H^3O^6Ag^3$, is an amorphous precipitate insoluble in hot water (Fittig). The acid obtained by the action of sulphuric acid on hydromellitic acid exhibits exactly the same characters.

Prehnitic acid, $C^{10}H^6O^8 = C^6H^2(CO^2H)^4$, is readily soluble in water, and crystallises from its concentrated solution in large prisms resembling the mineral prehnite. They contain 2 mol. water of crystallisation, which escapes on heating; the anhydrous acid melts at 237°–250°, with further loss of water and formation of the anhydride; the fused mass solidifies quickly at 220° into a crystalline mass, which resembles sal-ammoniac, and melts again at 239°. The aqueous solution of the acid gives with barium chloride a precipitate of small octohedral crystals, having the composition $(C^{10}H^5O^8)^2Ba$, and containing 3 or 4 mol. water of crystallisation. The methyl-ether of prehnitic acid crystallises in small thick concentrically grouped prisms, which melt at 104°–108°, solidify at 81°–70°, and sublime without decomposition. By the action of sodium-amalgam, the acid is converted into hydroprehnitic acid, a syrupy liquid, which on heating yields isophthalic acid, besides regenerated prehnitic acid.

Mellophanic acid, $C^{10}H^6O^8$, isomeric with prehnitic acid, is also readily soluble in water, and forms anhydrous crystalline crusts. From a solution containing a little hydrochloric acid it crystallises in fine prisms. Its aqueous solution is not precipitated by barium chloride. At 215° it begins to soften and to shrink together, and at 238° forms a clear liquid, the anhydride, which on cooling solidifies into crystals resembling frost-flowers and melting afterwards at 164°.

Prehnomalic acid, $C^{10}H^8O^9$, is formed in varying quantity, together with the two preceding, when the action of the sulphuric acid on hydromellitic acid is not carried on too long. It has the composition of prehnitic acid + water, and is easily transformed into the latter acid, by the further action of hot sulphuric acid, by the action of bromine-water, and by the action of methyl-iodide on its own silver salt, the methylic ether of prehnitic acid being then formed.

Prehnomalic acid is quadribasic; its aqueous solution evaporated over the water-bath leaves an amorphous mass, $C^{20}H^{14}O^{17}$, very soluble in water. The resulting solution soon solidifies to a magma of bulky needles having the composition $C^{20}H^{14}O^{17}.4H^2O$, only sparingly soluble in water. Prehnomalic acid dried at 100° melts at 210°, with loss of water, to a colourless liquid, and distils at a higher temperature, the distillate solidifying to a varnish-like mass which melts at 180°.

Hemimellitic acid, $C^9H^6O^6 = C^6H^3(CO^2H)^3$, is isomeric with trimesic acid, and is so called because it behaves when heated like mellitic acid, and contains only half as many atoms of carboxyl as the latter. To obtain it, the precipitate formed by adding baryta-water to the aqueous solution of the product resulting from the action of sulphuric acid on hydro-isopyromellitic acid is exhausted with cold water; the solution, containing barium hemimellitate mixed with small quantities of isopyromellitate and isophthalate, is mixed with sulphuric acid; the aqueous solution is again precipitated with baryta-water; and the filtered liquid is mixed with hydrochloric acid, which throws down hemimellitic acid in fine colourless needles, while isopyromellitic acid remains dissolved.

Hemimellitic acid melts at 185°, and if kept for some time at that temperature solidifies to a crystalline mass which melts at 125°. During the fusion long needles of phthalic anhydride sublime, together with a small quantity of benzoic acid. It is rather difficultly soluble in water, and crystallises slowly therefrom, a character by which it is distinguished from phthalic acid, which is also but slightly soluble, but crystallises quickly. It also differs from phthalic acid in being precipitated from its concentrated aqueous solution by hydrochloric acid.

The *ammonium salt* of hemimellitic acid is easily soluble in water, and crystallises in a radiate mass when evaporated on a watch-glass. A very dilute solution of the acid is not precipitated by *baryta-water*, but a strong solution gives a precipitate, thereby affording another distinction from phthalic acid, which is not precipitated by baryta-water. The solution of the ammonium salt gives with *barium chloride* a precipitate of microscopic needles consisting of the neutral salt, $(C^9H^3O^6)^2Ba^3 + 5H^2O$, which gives off 3 mol. water at 160°. The ammonium salt is not precipitated by *calcium chloride*, but alcohol added to the solution throws down flocks; its concentrated solution is precipitated by *cupric sulphate*. *Lead acetate* forms with the acid a flocculent precipitate sparingly soluble in excess of acetic acid. With *silver nitrate* in excess, the acid forms a flocculent precipitate which dissolves when heated, and separates in the granulo-crystalline form on cooling; this silver salt dried at 120° has the composition $C^9H^3Ag^3O^6$.

Pyromellitic Acid. $C^{10}H^6O^8 = C^6H^2(CO^2H)^4$ (iv. 762).—The anhydride of this acid, $C^{10}H^2O^6$, is produced by the dry distillation of mellitic acid:

$$C^{12}H^6O^{12} = 2CO^2 + 2H^2O + C^{10}H^2O^6,$$

and when boiled with water or alkalis, is converted, by assumption of water, into pyromellitic acid. Erdmann's method of preparing the acid by distilling sodium mellitate with sulphuric acid yields good results when only small quantities are operated on at once.

Pyromellitic acid bears a strong resemblance to phthalic acid. By distillation it yields the anhydride $C^{10}H^2O^6$, as an oil which quickly solidifies in large crystals and sublimes in long needles by slow evaporation. It dissolves easily in hot water, and is at the same time converted into the acid, much more easily than phthalic anhydride into phthalic acid. It melts at 286°, the acid at 264°; phthalic anhydride, on the other hand, melts at a lower temperature than phthalic acid.

Pyromellitic chloride, $C^6H^2(COCl)^4$, is produced by heating the acid for a considerable time with a slight excess of phosphorus pentachloride, and may be purified by redistillation in a stream of air at 180°. It then solidifies to a soft crystalline mass, which after a while becomes hard and brittle. It dissolves easily in pure ether, and when boiled with water is gradually reconverted into pyromellitic acid.

Ethylic pyromellitate, $C^6H^2(CO^2C^2H^5)^4$, obtained by heating the silver salt to 100° with ethyl iodide, crystallises from alcohol in short flat needles, insoluble in water, melting at 53°, and subliming in needles at a higher temperature. It is probably also one of the products of the dry distillation of ethylic hydromellitate (p. 810).

Hydropyromellitic acid, $C^{10}H^{10}O^8 = C^6H^6(CO^2H)^4$, is produced by the action of sodium-amalgam on the ammonium salt of pyromellitic acid, the reduction, if assisted by a gentle heat, being complete in three or four weeks. It remains on evaporation as a colourless syrup, which gradually solidifies in the crystalline form. The presence of alkali interferes with its crystallisation. It is hygroscopic, but not deliquescent; very soluble in water. When heated, it melts with intumescence to a colourless liquid, which decomposes when further heated. With *barium acetate*, the acid forms no precipitate in the cold; but on heating, a flocculent powder is precipitated, which quickly disappears on cooling. *Baryta-water* forms an amorphous precipitate which shrinks together to some extent when heated. *Manganous acetate* forms no precipitate in the cold, but at the boiling heat a flocculent precipitate which disappears immediately on cooling. Altogether hydropyromellitic acid reacts just like hydromellitic acid, excepting that its salts are somewhat more soluble.

Hydropyromellitic acid heated with 5 pts. of strong sulphuric acid gives off large quantities of carbonic and sulphurous anhydrides, yields a small sublimate of benzoic acid, but no phthalic anhydride, and a residue consisting of pyromellitic acid, trimellitic acid, isomeric with hemimellitic acid, and isophthalic acid. To separate these acids, the residual mass is diluted with water and exhausted with ether, and the aqueous solution of the ethereal extract is precipitated with boiling baryta-water, whereby pyromellitic and trimellitic acids are precipitated, while isophthalic acid remains in solution. The precipitate is decomposed by sulphuric acid, the filtrate concentrated, and the crystalline mass which separates on cooling is fused and digested with pure ether, which dissolves the trimellitic acid, leaving the pyromellitic acid undissolved.

The decomposition of hydropyromellitic acid by sulphuric acid may be represented by the following equation:

$$C^{10}H^{10}O^8 + 2SO^4H^2 - 4H^2O - 2SO^2 = \begin{cases} C^{10}H^6O^8, & \text{Pyromellitic acid} \\ CO^2 + C^9H^6O^6, & \text{Trimellitic acid} \\ 2CO^2 + C^8H^6O^4, & \text{Isophthalic acid.} \end{cases}$$

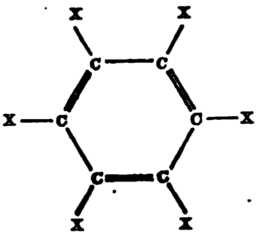
Trimellitic Acid. $C^9H^6O^6 = C^6H^3(CO^2H)^3$.—This acid, dissolved as above by ether, is purified by conversion into a lead salt in the manner already described (p. 811). It is moderately soluble in water and ether, and crystallises from aqueous solution by slow evaporation in nodular groups of indistinct crystals. It melts at 216°, and when more strongly heated does not sublime, but distils in oily drops, which solidify on cooling to nodular groups of concentric needles. In this respect it bears considerable resemblance to isopyromellitic acid, which however melts at 238°, and solidifies from the oil obtained on distilling it, in needles and isolated crystals. These characters, however, are distinctly exhibited only when the respective acids are pure. The two acids are further distinguished by the different solubilities of their barium salts, isopyromellitic acid giving a precipitate with barium chloride, whereas this reagent does not produce a precipitate even with the ammonium salt of trimellitic acid.

Ammonium trimellitate is easily soluble in water, and crystallises in concentric needles from the concentrated solution. The *barium salt* is sparingly soluble, and separates on mixing the ammonium salt with barium chloride, especially on heating, in crystalline nodules, exhibiting, after drying over sulphuric acid, the composition $(C^9H^5O^6)^2Ba + 3H^2O$. With *lead acetate*, trimellitic acid forms a flocculent precipitate nearly insoluble in acetic acid. *Silver nitrate* forms, especially on addition of ammonia, a granular precipitate, which dissolves when heated, and reappears on cooling.

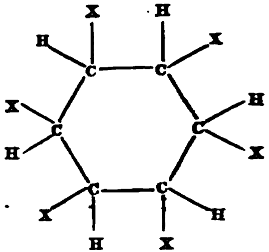
The acids above described belong to two classes, the benzocarbonic and the hydrobenzocarbonic acids. Of the benzocarbonic acids, as already observed, twelve are possible, and eleven have actually been obtained. These are arranged by Baeyer as ortho-, meta-, and para- compounds (AROMATIC SERIES, p. 197) as follows:

	Ortho-series.	*Meta-series.*	*Para-series.*
$C^6(CO^2H)^6$	1 2 3 4 5 6 Mellitic acid.		
$C^6H(CO^2H)^5$	1 2 3 4 5 Unknown.		
$C^6H^2(CO^2H)^4$	1 2 3 4 Mellophanic acid.	1 2 3 5 Prehnitic.	1 2 4 5 Pyromellitic acid.
$C^6H^3(CO^2H)^3$	1 2 3 Hemimellitic acid.	1 2 4 Trimesic acid.	1 3 5 Trimellitic acid.
$C^6H^4(CO^2H)^2$	1 2 Phthalic acid.	1 3 Isophthalic acid.	1 4 Terephthalic acid.
$C^6H^5CO^2H$	1 Benzoic acid.		

Of the hydrobenzo-carbonic acids, two were previously known, viz. hydrobenzoic acid, $C^7H^{10}O^2$, and hydrophthalic acid, $C^8H^8O^4$; and four more have been added to the list by Baeyer's recent investigations, viz. hydromellitic acid, $C^{12}H^{12}O^{12}$, hydropyromellitic, hydroprehnitic, and hydromellophanic acids, $C^{10}H^{10}O^8$. The difference of structure of mellitic and hydromellitic acid may be represented by the following formulæ, in which the symbol X stands for CO^2H:



Mellitic.



Hydromellitic.

In the first, the nucleus C^6 consists, as in most aromatic compounds, of three pairs of carbon-atoms united by two affinities, while each pair is united with the next by only one affinity. In the second the six carbon-atoms are united together by only one affinity.

The stability of the hydro-acids increases in a remarkable manner with the number of the carboxyl groups; for whereas hydrobenzoic acid loses its hydrogen by mere exposure to the air, and hydrophthalic acid is so unstable that it reproduces phthalic acid and benzoic acid under the influence of almost all reagents, isohydromellitic acid is so stable that it is not oxidised even by a mixture of strong sulphuric and fuming nitric acids.

MENAPHTHOXYLIC ACID. Syn. with Naphthalene-carboxylic Acid.

MENAPHTHYLAMINE. $C^{11}H^{19}NH^2$.—A base produced by treating menaphthothiamide, $C^{11}H^9NS$, in alcoholic solution with hydrochloric acid and zinc, as long as hydrogen sulphide is given off. It is a liquid boiling at 290°–293°, and rapidly absorbing carbonic acid from the air. The hydrochloride, $C^{11}H^{19}NH^2.HCl$, crystallises in long, sparingly soluble needles; the platinochloride, $2(C^{11}H^{19}NH^2.HCl).PtCl^4$, is a yellow crystalline precipitate. The sulphate and nitrate crystallise well. With carbon bisulphide the base forms a white crystalline mass. With alcoholic soda and chloroform it forms the strongly smelling compound formomenaphthyl nitrile (Hofmann, *Deut. chem. G. Berlin.* 1868, p. 100; *Zeitschr. f. Chem.* [2] iv. 503).

MENEGHINITE. $4PbS.Sb^2S$.—According to G. vom Rath (*Pogg. Ann.* clxxxii. 372; *Jahresb.* 1867, 974), the crystalline form of this mineral is not trimetric, as found by Sella (iii. 879), but monoclinic. In the primary form the ratio of the clinodiagonal: orthodiagonal: principal axis = 0·361639 : 1 : 0·116825. Angle of inclined axes = 92° 19′ 42″.

MENHADEN OIL (Warren a. Storer, *Mem. Amer. Acad.* [new series] ix. 177; *Zeitschr. f. Chem.* [2] iv. 228).—The oil obtained from *Alosa Menhaden*, a species of herring, forms a lime-soap which, when distilled with excess of lime, yields the following volatile hydrocarbons:

		Boiling point of the fraction	Amount in the crude oil
Amylene	C^5H^{10}	35°–37°	0·8 p. c.
Quintane or Amyl hydride	C^5H^{12}	37°–41°	
Hexylene . . .	C^6H^{12}	65°–66°	3·9 „
Hexane	C^6H^{14}	67·5°–68°	2·8 „
Benzene	C^6H^6	80°–81°	3·1 „
Heptylene . . .	C^7H^{14}	93°–94°	4·7 „
Heptane	C^7H^{16}	97·8°	7·6 „
Toluene	C^7H^8	110°–111°	6·9 „
Octylene	C^8H^{16}	121°–122°	12·5 „
Octane	C^8H^{18}	128°–129°	
Xylene	C^8H^{10}	140°–144°	13·3 „
Nonylene . . .	C^9H^{18}	153°	7·8 „
Decylene	$C^{10}H^{20}$	165°–174°	23·5 „
Isocumene . . .	C^9H^{12}		
Undecylene . . .	$C^{11}H^{22}$	193°–196°	10·2 „
Duodecylene . . .	$C^{12}H^{24}$	208°–213°	3·1 „

MENYANTHIN. Kromayer (*Arch. Pharm.* [2] cxxiv. 37; *Jahresb.* 1865, p. 610) recommends certain modifications of the process originally given for the preparation of this compound from *Menyanthes trifoliata*; he now assigns to it the formula $C^{30}H^{46}O^{14}$, with variable amount of water. The sugar formed in the decomposition of menyanthin by acids is dextroglucose, $C^6H^{12}O^6 . 6H^2O$. The volatile product of the reaction, menyanthol, is represented by the formula C^8H^8O (which, however, does not agree well with the analysis), and the decomposition is represented by the equation

$$C^{30}H^{48}O^{15} = C^6H^{12}O^6 + 3C^8H^8O + 6H^2O.$$

By exposure to the air, and by fusion with potash, menyanthol is converted into a crystalline sublimable acid.

MERCURACETYL OXIDE. See Acetylene (p. 36).

MERCURAMMONIUMS (Weyl, *Pogg. Ann.* cxxi. 601; cxxxi. 524; *Zeitschr. f. Chem.* [2] iv. 129; *Jahresb.* 1864, p. 282; 1867, p. 306)—Hydrated dimercurammonium oxide, $(NHg^2)^2O . 3H^2O$, is obtained by passing dry ammonia gas over amorphous mercuric oxide, or more quickly by the action of ammonia on mercuric oxide under pressure in the apparatus described under Sodammonium (v. 328), one arm of the tube containing silver chloride saturated with ammonia, the other mercuric oxide; also by treating the oxide with an alcoholic solution of ammonia for several hours, and drying the product at ordinary temperatures. The product obtained by either of these processes has, if formed in the dark, the same yellow colour as precipitated mercuric oxide; if it has been exposed to light during its formation, it has a lighter colour, and leaves mercurous chloride when dissolved in hydrochloric acid; by prolonged exposure to the light, it suffers further decomposition and yields metallic mercury. It is decomposed by water or dilute sulphuric acid, giving up ammonia, and being converted into a white insoluble substance. In warm hydrochloric or nitric acid it dissolves, with formation of the corresponding mercury and ammonium compounds. Heated in a flame on platinum foil, it detonates with great violence. When heated in a stream of dry ammonia gas, it gives off 2 mol. water at 80°, leaving a light brown monohydrate, and at 100°, the remaining molecule, leaving the dark brown anhydrous oxide $(NHg^2)^2O$. This anhydrous oxide detonates by heat, percussion, or friction. In contact with water it assumes a lighter colour, but the water at the same time takes up ammonia. The trihydrate may also be converted into the anhydrous oxide by treating it with ammonia under such a pressure that the compound may be surrounded for a long time with liquid ammonia.

The corresponding haloïd compounds cannot be prepared by treating the oxide with aqueous acids, and only in an impure state by the use of alcoholic solutions of the acids. When mercuric chloride or iodide is subjected to the action of liquefied ammonia, in the apparatus above mentioned, a monomercuro-diammonium compound is first produced, which afterwards dissolves in ammonia, and on evaporation of the excess of ammonia, yields a crystalline mass, which, according to the observed increase of weight, may be regarded either as a monomercuro-diammonium compound, or as a dimercurammonium compound mixed with ammonium salt, its formation being represented by the equation

$$2HgCl^2 + 4NH^3 = 2N^2H^6\overset{\prime\prime}{Hg}Cl \text{ or } N\overset{\prime\prime}{Hg}{}^2Cl + 3NH^4Cl.$$

These compounds do not, however, admit of purification. Better results are obtained by the use of mercuric oxychloride or oxyiodide. The oxychloride (obtained by heating a mixture of 3 mol. mercuric oxide with 1 mol. of the chloride to above 100°) yields *dimercurammonium chloride* in the form of a yellow body insoluble in excess of liquid ammonia:

$$3HgO . HgCl^2 + 8NH^3 = 2NHg^2Cl + 3(NH^4)^2O.$$

This chloride, heated to 300°, is resolved into mercurous chloride, metallic mercury, and nitrogen; it is not attacked by water, either cold or boiling; is dissolved by cold hydrochloric acid after prolonged contact; decomposed by cold potash-ley with formation of potassium chloride and yellow explosive dimercurammonium oxide, and by boiling potash-ley or potassium chloride with evolution of ammonia and formation of mercuric oxychloride or chloride.

Mercuric oxyiodide, $3HgO . HgI^2$, similarly treated yields a brown non-explosive product, which when freed from excess of ammonia by heating to 100° in a stream of dry air, has the composition of *dimercurammonium iodide*, and resembles the chloride in its properties. The corresponding *bromide* and *cyanide* have also been obtained; the cyanide is highly explosive. Mercuric oxychloride or oxyiodide heated in a stream of ammonia gas is converted into *amidated oxychloride*, $NH^2Hg^2ClO = NH^2HgCl.HgO$, or *oxyiodide*, $NH^2HgI.HgO$, which again are converted by the action of liquid ammonia in a sealed tube into dimercurammonium compounds; *e.g.*,

$$NH^2HgCl.HgO + 2NH^3 = NHg^2Cl + (NH^4)^2O.$$

MERCURIALINE. This name is given by Reichardt (*J. pr. Chem.* civ. 301; *Zeitschr. f. Chem.* [2] iv. 734) to a volatile base having the composition of methylamine, which is obtained, together with ammonia, by distilling the seeds or other parts of *Mecurialis annua* or *M. perennis* with lime or potash and water. It is described as liquid at ordinary temperatures, and strongly alkaline, and its sulphate and oxalate are said to differ from those of methylamine; but it is probably nothing but impure methylamine.

MERCURY. The boiling point of mercury under a pressure of 760 mm. is 357·25° (Regnault, *Relation des Expériences*, &c.). Its specific gravity at 4°, reduced to a vacuum and compared with that of water at 4°, is 13·594 (Balfour Stewart, *Proc. Roy. Soc.* xv. 10); this determination agrees with those of Regnault and Kopp (iii. 584).

Its heat-conducting power in the liquid state is 53·5 according to Calvert a. Johnson (*Jahresb.* 1864, p. 169); 35·4 according to Gripon (*Phil. Mag.* [4] xxxiii. 547); that of silver being = 1000. Its coefficient of cubical expansion is 0·0001812 (Matthiessen, *Proc. Roy. Soc.* xiv. 551). (See HEAT, p. 671.) Regnault's experiments gave 0·00018153.

Amalgams. According to Cailletet (*Bull. Soc. Chim.* [2] viii. 299) the amalgamation of metals (including the zinc cylinders of galvanic batteries) may be easily effected by dipping them into sodium-amalgam containing 0·5 p. c. sodium.

Calvert a. Johnson (*loc. cit.*) have found the following values for the heat-conducting powers of solid amalgams (silver = 1000):

$HgSn^2$	272·1	$HgZn^2$	304·1	$HgBi^4$	67·4
$HgSn^3$	296·3	$HgZn^3$	315·0	$HgBi^6$	81·5
$HgSn^4$	302·5	$HgZn^4$	378·7	$HgBi^8$	79·9
$HgSn^5$	332·3	$HgZn^5$	409·1	$HgBi^{10}$	73·7

Liquid amalgams containing excess of mercury were found to differ but little in heat-conducting power from pure mercury, although the percentage of tin varied from 10·5 to 22·95, that of zinc from 6·09 to 13·97, that of bismuth from 17·55 to 34·73.

Magnesium-amalgam is formed, according to Wanklyn a. Chapman (*Chem. Soc. J.* [2] iv. 141), by contact of mercury with magnesium free from oxide, slowly in the cold, quickly and with violence when the two metals are heated to the boiling point of mercury. In this amalgam the affinities of the magnesium are exalted, contrary to what takes place in the case of sodium-amalgam. Magnesium-amalgam containing 0·5 p. c. magnesium swells up instantly in contact with the air, and loses its lustre, decomposes water with violence, and more rapidly than sodium-amalgam containing twice that percentage of sodium.

Phipson (*Bull. Soc. Chim.* [2] v. 243) observed that when 207 pts. *lead*, 118 *tin*, 284 *bismuth*, and 1617 mercury were mixed together, the temperature of the amalgam fell from +17° to −10°.

Sodium-Amalgam.—This compound easily reduces mercuric chloride, auric chloride, and the haloïd compounds of silver when laid in a thin slice on the pulverised substance placed in a test-tube together with a little water. Ferric chloride is partly reduced to ferrous chloride, partly to metallic iron, and with a sufficient quantity of the amalgam, completely to metal, which remains as iron-amalgam. Chromic chloride suspended in very dilute hydrochloric acid is reduced in like manner to liquid, easily decomposible chromium-amalgam, the liquid turning green before complete reduction takes place. Sodium-amalgam is well adapted for the reduction of chloride, iodide, and bromide of silver. It acts but slowly on an ethereal solution of ferric chloride, and not at all on silver chloride under rock-oil (Bunge, *Chem. Centr.* 1865, p. 257).

Bromiodide. $HgIBr$.—Produced by heating mercuric bromide dissolved in acetone with an alcoholic iodide; also by crystallising mercuric bromide and iodide together from solution in ether or acetone; and by adding iodine to a solution of the bromide in acetone. Forms beautiful yellow crystals melting at 229°, subliming without decomposition, and separating in scales from solution in ether, without alteration of colour (Oppenheim, *Deut. chem. Ges. Ber.* 1869, 571; *Zeitschr. f. Chem.* [2] v. 155).

Chlorides. For the preparation of *mercuric chloride* on the large scale, Wagner (*Dingl. pol. J.* clxxxvi. 135) recommends: (*a*) Decomposition of basic mercuric sulphate (*mineral turpethum*) by heating it with hydrochloric acid, whereupon mercuric chloride separates and sulphuric acid passes into solution (the acid liquid yields by evaporation a sulphuric acid containing mercuric oxide, and adapted for dissolving mercury).—(*b*) Digestion of the yellow mercuric oxide precipitated by caustic soda from the nitrate with magnesium chloride (the mother-liquor of the working of carnallite), the reaction being represented by the equation: $HgO + MgCl^2 = HgCl^2 + MgO$. If the presence of potassium chloride in the mercuric chloride is not objectionable, the solution of the carnallite may be directly saturated with mercuric oxide. After the separation of the precipitated magnesia, the liquid yields by evaporation the salt $KCl.HgCl^2 + H^2O$. Wagner observes that this salt may be used just as well as pure mercuric oxide for the preparation of rosaniline salts.

Mercuric chloride prepared by sublimation in an atmosphere of hydrochloric acid gas is quite free from calomel. It may be obtained by dissolving 10 pounds of mercury in 12·5 pounds of sulphuric acid of 66° Bm., carefully evaporating the liquid, and subliming the residual mass of neutral and acid mercuric sulphate with 9 pounds of sodium chloride (H. Fleck, *Bull. Soc. Chim.* [2] viii. 39).

According to Bonnewyn (*ibid.* iv. 201), the presence of an extremely small proportion of corrosive sublimate in calomel may be detected by immersing a clean knife-blade in the calomel moistened with alcohol or ether. If only $\frac{1}{50000}$ part of corrosive sublimate is present, a black spot will be formed on the steel, very difficult to remove by friction, whereas if the calomel is pure no such spot will be formed.

Debray (*Compt. rend.* lxvi. 1339) finds that gold-leaf heated in vapour of *calomel* to 440° retains its lustre and malleability, whereas when heated in vapour of mercuric iodide to the temperature at which that compound suffers dissociation it becomes white and friable. Hence Debray concludes that mercurous chloride at 440° (the temperature at which Deville a. Troost determined its vapour-density) is not resolved into metallic mercury and mercuric chloride, and that therefore its abnormal vapour-density (for the formula Hg^2Cl^2) does not result from dissociation. On the other hand, Erlenmeyer and Odling find that gold-leaf immersed in calomel vapour heated to about the boiling point of mercury becomes amalgamated, showing that the mercurous chloride is at least partly decomposed, with separation of mercury. Erlenmeyer observes, however, that this decomposition cannot decide the question as to the molecular weight of mercurous chloride, inasmuch as it may take place either in the manner represented by the equation $Hg^2Cl^2 = HgCl^2 + Hg$, or $HgCl + HgCl = HgCl^2 + Hg$ (*Jahresb.* 1864, p. 280).

Iodide. According to Oppenheim (*Zeitschr. f. Chem.* [2] vi. 156), mercuric iodide passes from the red to the yellow modification at a temperature between 148° and 154°, probably nearer to the former.

Oxides. *Mercuric oxide* added to melting potassium hydrate dissolves without evolution of gas; and if the addition be continued not quite to saturation, the mass then slowly cooled and lixiviated with water, a heavy violet crystalline powder is obtained, consisting of $K^2O.HgO$, and a lighter grey-green powder of variable composition, containing from 2 to 5 p. c. potash. Similar results are obtained with sodium hydrate (St. Meunier, *Compt. rend.* lx. 557, 1232; *Jahresb.* 1865, p. 277).

Fonberg (*Ann. Ch. Phys.* [4] i. 300) finds, contrary to the statement of H. Rose (iii. 909), that alkalis and alkaline earths are separated by mercuric and by mercurous oxide, when the saturated solutions of their haloïd salts in large excess are agitated or boiled with the oxide; the decomposition is facilitated by passing carbon dioxide through the solution. The oxygen-salts of these bases are also decomposed in this manner, but with much greater difficulty. These reactions appear also to have been observed by Melsens in 1849 (*Ann. Ch. Phys.* [3] xxvi. 220), who likewise found that a neutral or slightly acid solution of potassium iodide becomes alkaline by agitation with air and metallic mercury together.

Sulphides. When a mercuric double salt, *e.g.* ($2KCyS.HgCy^2S^2$ or $2NaCl.HgCl^2$), is heated with an equivalent quantity of *sodium hyposulphite*, black mercuric sulphide is precipitated as soon as the liquid becomes acid; if the hyposulphite is used in excess, the mercuric sulphide separates in the form of cinnabar as long as the liquid remains neutral; but on heating it above 60°, the black sulphide makes its appearance as soon as the liquid acquires an acid reaction. The reaction in the acid solution (*a*), and in the neutral solution (*b*), may be represented by the following equations:

$$(a)\quad HgCl^2 + Na^2S^2O^3 = HgS + 2NaCl + SO^3$$
$$(b)\quad HgCl^2 + 2Na^2S^2O^3 = HgS + 2NaCl + Na^2S^3O^6$$

The formation of cinnabar under the conditions above mentioned does not take place in presence of strontium, calcium, or magnesium salts, but is accelerated by copper or zinc salts. When 1 mol. mercuric chloride is mixed with 4 mol. sodium hyposulphite and 4 mol. zinc sulphate in very dilute solution, and the mixture is heated to 45° or 50° for about sixty hours, three-fourths of the mercury is separated from the neutral liquid as dark red crystalline cinnabar, the rest at a higher temperature as black amorphous sulphide. If barium chloride be used instead of zinc sulphate, barium sulphate separates together with the cinnabar. In the ordinary mode of preparing cinnabar in the wet way, the transformation of the amorphous sulphide depends upon its successive solution in the alkaline sulphide, from which it separates in the crystalline form. The presence of sodium hyposulphite does not facilitate, but rather hinders this transformation (H. Fleck, *J. pr. Chem.* xcix. 247).

The solubility of mercuric sulphide in the sulphides of the alkali-metals and alkaline-earth metals may be made available for the extraction of the sulphide from its gangue, and especially for the valuation of poor cinnabar ores (containing 2 to 3 p. c. cinnabar). The best solvent for the purpose is a solution of barium sulphide, containing about 50 grms. of barium in a litre, obtained by dissolving crude barium sulphide in water, and crystallising out the greater part of the barium hydrate. The mercuric sulphide is precipitated from the solution of hydrochloric acid (whereby barium chloride is obtained as a secondary product), and decomposed in the ordinary way. For the assay of poor bituminous ores, the bituminous matter must first be extracted by benzol, the ore then well dried and exhausted with barium sulphide, and the precipitate thrown down by hydrochloric acid freed from admixed sulphur by digestion with carbon bisulphide (Wagner, *J. pr. Chem.* xcviii. 23; *Jahresb.* 1866, p. 834).

Cinnabar digested for a day with excess of a solution of *iodine in potassium iodide* is converted into potassio-mercuric iodide: $HgS + 2KI + I^2 = 2KI.HgI^2 + S$. The diminution of the free iodine affords a measure of the quantity of mercury dissolved (Wagner, *loc. cit.*).

The black precipitate formed in mercurous salts by *hydrogen sulphide*, or colourless *ammonium sulphide*, is not a definite compound, but a mixture of mercury and mercuric sulphide, from which nitric acid extracts the metallic mercury, forming either a mercurous or a mercuric salt, and in the latter case the white double compound $Hg(NO^3)^2.2HgS$. This double compound is nearly insoluble in nitric acid, and forms with hydrochloric acid the yellow compound $HgCl^2.2HgS$, which decomposes when heated in the liquid, with formation of sulphuric acid and separation of sulphur; sulphuric acid of medium strength converts it into the white salt, $HgSO^4.2HgS$. Mercuric sulphide, which under ordinary circumstances is insoluble in nitric acid, is likewise converted by prolonged heating with that acid into the white compound $Hg(NO^3)^2.2HgS$. Mercuric sulphide is insoluble in sodium sulphydrate, and consequently its solution in sodium sulphide is precipitated by hydrogen sulphide or ammonium sulphydrate. It appears from the preceding that the separation of mercury as sulphide from other sulphides of the same group by nitric acid is exact only when the mercury is present as mercuric sulphide (Barfoed, *Bull. Soc. Chim.* [2] iii. 183).

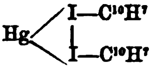
MERCURY-RADICLES, ORGANIC. *Mercuric ethide* is rapidly decomposed at temperatures near its boiling point by carbon oxysulphide, metallic mercury being separated, and a liquid having a strong alliaceous odour being formed, probably ethyl thiopropionate (Than, *Zeitschr. f. Chem.* [2] iv. 56).

Mercuric acetoxymethide, $C^3H^6O^2Hg = Hg\left\{\begin{matrix}C^2H^3O^2\\CH^3\end{matrix}\right.$, is produced by heating mercuric methide with acetic acid to 120°–130° in a sealed tube. It crystallises from hot glacial acetic acid in shining, white, thin, rhombic tables, melting at 142°–143°, having an offensive and very persistent odour, nearly insoluble in boiling water and cold acetic acid, more soluble in hot acetic acid and in alcohol. It volatilises with vapour of water, and reacts with hydrochloric acid, ammonium sulphide, and iodine, like the corresponding compounds of the aromatic series described below. *Mercuric acetoxethide* resembles the methyl-compound, and melts at 178° (Otto, *Zeitschr. f. Chem.* [2] vi. 25).

Mercuric Naphthylide. $Hg(C^{10}H^7)^2$ (Otto a. Möries, *Ann. Ch. Pharm.* cxlvii. 164; *Zeitschr. f. Chem.* [2] iii. 377; iv. 162; *Jahresb.* 1867, p. 715).—This compound is easily and abundantly formed by the action of sodium-amalgam on monobromonaphthalene:

$$2C^{10}H^7Br + Na^2Hg = Hg(C^{10}H^7)^2 + 2NaBr.$$

A solution of bromonaphthalene in several times its volume of coal-tar naphtha boiling between 120° and 140° is boiled for about nineteen hours with pasty sodium-amalgam, in a flask having an upright condenser, and the liquid is filtered hot, whereupon the mercuric naphthide crystallises out almost completely. After recrystallisation from benzol or carbon bisulphide, it forms small white crystals, appearing under the microscope as rhombic prisms terminated by four-sided pyramids. It is inodorous, unaffected by air and light, insoluble in water, slightly soluble in boiling alcohol, cold benzol, or ether, more easily in hot carbon bisulphide, chloroform, and benzol. It melts at 243° and decomposes at a higher temperature, depositing small quantities of charcoal and mercury, and yielding an oily crystallising distillate. By ignition with soda-lime it yields naphthalene, together with another hydrocarbon crystallising in canary-yellow laminæ, and melting at 133°. Heated with concentrated hydriodic, hydrobromic, or hydrochloric acid, it is resolved into naphthalene and mercuric iodide, bromide, or chloride. With iodine it unites directly, forming naphtho-mercuric di-iodide, $(C^{10}H^{7})^{2}HgI^{2}$, which on further addition of iodine is resolved into mercuric iodide and iodonaphthalene, $C^{10}H^{7}I$.

Naphthomercuric Di-iodide, $(C^{10}H^{7})^{2}HgI^{2}$ = 
$Hg\left\langle \begin{array}{l} I—C^{10}H^{7} \\ \mid \\ I—C^{10}H^{7} \end{array}\right.$ (the iodine being trivalent), is prepared by mixing the solutions of 1 mol. mercuric naphthylide and 1 mol. iodine in carbon bisulphide, distilling off the latter, and recrystallising the residue from hot alcohol. It forms soft satiny needles or dendritic groups, not altered by light, insoluble in water, slightly soluble in hot alcohol, chloroform, benzol, and carbon bisulphide, melting at 185°, and resolved by ignition with lime into naphthalene, iodine, and mercuric oxide.

Bromine acts on mercuric naphthylide in the same manner as iodine, forming in the first instance a crystallisable dibromide, which is decomposed by more bromine into bromonaphthalene and mercuric bromide.

Mercuric Acetoxynaphthlyide, $C^{12}H^{10}HgO^{2}$ =
$Hg\left\{\begin{array}{l} C^{10}H^{7} \\ OC^{2}H^{3}O \end{array}\right.$, is produced, together with naphthalene, by heating mercuric naphthylide with excess of glacial acetic acid:

$$Hg(C^{10}H^{7})^{2} + HOC^{2}H^{3}O = C^{10}H^{8} + Hg(C^{10}H^{7})(OC^{2}H^{3}O).$$

On mixing the solution with a large quantity of hot water, and crystallising the resulting white precipitate from hot alcohol, naphthalene separates out, while mercuric acetoxynaphthylide remains in solution, and may be obtained by evaporation, prolonged heating, and recrystallisation. It is insoluble in water, easily soluble in hot glacial acetic acid, alcohol, carbon bisulphide, benzol, and chloroform, less soluble in ether; crystallises in small needles appearing under the microscope as flat rhombic prisms or tables; melts at 154°, and decomposes at a higher temperature, depositing charcoal, and yielding an oily distillate which quickly solidifies. With hydrochloric, hydriodic acid, &c., it reacts like mercuric naphthylide. It is not decomposed by heating with water to 140°, with ethyl iodide to 160°, or by sodium-amalgam, zinc, copper, or tin at ordinary temperatures; neither does it unite with mercuric chloride.

Mercuric Phenylide. $Hg(C^{6}H^{5})^{2}$ (Dreher a. Otto, *Zeitschr. f. Chem.* [2] iv. 685; vi. 9).—This compound is prepared, like the naphthylide, by heating a mixture of monobromobenzene and anhydrous benzol (B. P. 100°–120°–140°) with pasty sodium-amalgam; the reaction may, however, be considerably facilitated by addition of a little acetic ether ($\frac{1}{10}$ of the weight of the bromobenzene).

Mercuric phenylide crystallises from a hot-saturated benzol-solution in small, white, vitreous, asbestos-like needles; from a dilute solution in white rhombic prisms often united in tufts. It is insoluble in water, easily soluble in chloroform, carbon bisulphide, and benzol, less easily in ether and boiling alcohol, slightly in cold alcohol. Melts at 120°; sublimes without decomposition when cautiously heated in small quantities; boils when heated above 300°, and distils, with formation of benzene and diphenyl, and separation of mercury and charcoal; probably thus:

$$3Hg(C^{6}H^{5})^{2} = 5C^{6}H^{6} + Hg^{3} + C^{6}$$

and

$$2C^{6}H^{6} = C^{12}H^{10} + H^{2}.$$

It is quickly decomposed by dry *hydrochloric acid gas*, or by heating with the concentrated aqueous acid, into benzene and mercuric chloride:

$$Hg(C^{6}H^{5})^{2} + 2HCl = 2C^{6}H^{6} + HgCl^{2};$$

and reacts in a similar manner with hydriodic, hydrobromic, nitric, sulphuric acid, &c.

Heated with 2 at. *sulphur* above the melting point of the latter, it yields mercuric sulphide and phenyl sulphide, together with a small quantity of phenyl sulphydrate:

$$Hg(C^6H^5)^2 + S^2 = HgS + (C^6H^5)^2S.$$

A solution of mercuric phenylide in alcohol or carbon bisulphide acted upon by 2 at. *iodine* yields phenyl iodide and mercuric iodophenylide:

$$Hg(C^6H^5)^2 + I^2 = C^6H^5I + Hg\left\{\begin{matrix}C^6H^5\\ I\end{matrix}\right..$$

With 4 at. iodine the products are phenyl iodide and mercuric iodide:

$$Hg(C^6H^5)^2 + I^4 = 2C^6H^5I + HgI^2.$$

Mercuric Iodophenylide crystallised from boiling benzol, or a mixture of benzol and absolute alcohol, forms white satiny rhombic tables, not altered by light, melting at 265°–266°, insoluble in water, nearly insoluble in cold alcohol, ether, and benzol, more easily in hot benzol or chloroform, still more in carbon bisulphide. Heated above its melting point, it partly sublimes unaltered, and is partly decomposed, with separation of mercuric iodide.

Mercuric Bromophenylide, $Hg\left\{\begin{matrix}C^6H^5\\ Br\end{matrix}\right.$, obtained in like manner, resembles the iodine-compound in the form and lustre of its crystals, and in its relations to solvents; melts at 291°; and is converted by excess of bromine into mercuric bromide and phenyl bromide.

Mercuric Chlorophenylide is obtained by slowly passing chlorine, not in excess, over mercuric phenylide, or into a solution of that compound in carbon bisulphide; more easily, however, by heating mercuric phenylide with mercuric chloride to 110° in sealed tubes: $Hg(C^6H^5)^2 + HgCl^2 = 2Hg\left\{\begin{matrix}C^6H^5\\ Cl\end{matrix}\right.$. The iodine and bromine derivatives may be obtained in a similar manner. Mercuric chlorophenylide resembles the two preceding compounds, and is likewise decomposed in a similar manner, though less readily, by excess of chlorine. Hypochlorous acid acts upon mercuric phenylide in the same manner as free chlorine.

Nascent hydrogen, evolved by sodium-amalgam in alcoholic solution, converts mercuric iodophenylide into mercuric phenylide; thus:

$$2Hg(C^6H^5)I + H^2 = 2HI + Hg + Hg(C^6H^5)^2.$$

In contact with anhydrous benzol, *sodium-amalgam* acts upon mercuric iodophenylide in the same manner as nascent hydrogen:

$$2Hg(C^6H^5)I + Na^2 = 2NaI + Hg + Hg(C^6H^5)^2;$$

but *free sodium* unites with the mercury of the phenyl-compound, producing sodium-amalgam, sodium-iodide being also formed, together with a brown organic product which does not dissolve in the ordinary solvents.

Mercuric bromophenylide, boiled for some time with alcoholic solution of *potassium sulphide*, is decomposed in the manner shown by the equation:

$$2Hg(C^6H^5)Br + K^2S = 2KBr + HgS + Hg(C^6H^5)^2.$$

Mercuric Acetoxyphenylide, $Hg\left\{\begin{matrix}C^6H^5\\ C^2H^3O^2\end{matrix}\right.$, is formed, like the corresponding naphthyl-compound, by boiling mercuric phenylide with several times its volume of strong acetic acid:

$$Hg(C^6H^5)^2 + C^2H^4O^2 = C^6H^6 + Hg\left\{\begin{matrix}C^6H^5\\ C^2H^3O^2\end{matrix}\right..$$

The product separated from the solution by water and crystallised from hot water, forms small, white, inodorous, vitreous, rhombic prisms, mostly in radiate groups; melting at 140°, slightly soluble in cold water, more easily in hot water, strong acetic acid, benzol, and alcohol. Similar compounds are formed with *acetic* and *propionic acids*.

Mercuric acetoxyphenylide is decomposed by distillation, yielding benzene, acetic anhydride, acetic acid, and diphenyl, together with free carbon and mercury. Boiled with aqueous *hydrochloric acid*, it yields mercuric chloride, benzene, and acetic acid:

$$Hg(C^6H^5)(C^2H^3O^2) + 2HCl = HgCl^2 + C^6H^6 + C^2H^4O.$$

Hydriodic, sulphuric, and other acids act in a similar manner. With nascent *hydrogen*, generated by sodium-amalgam in the alcoholic solution, it yields mercury, benzene, and acetic acid:

$$Hg(C^6H^5)(C^2H^3O^2) + H^2 = Hg + C^6H^6 + C^2H^4O^2.$$

In aqueous solution it is decomposed by *iodine*, yielding mercuric iodide, phenyl iodide, acetic acid, and iodic acid. Perhaps Schützenberger's acetate of iodine, $(C^2H^3O)IO$ (p. 25), is first formed:

$$Hg(C^6H^5)(C^2H^3O^2) + I^4 = HgI^2 + C^6H^5I + (C^2H^3O)IO;$$

and then decomposed by the water, in the manner shown by the equation:

$$3(C^2H^3O)IO + 3H^2O = 2HI + IHO^3 + 3C^2H^4O^2.^*$$

An alcoholic solution of mercuric acetoxyphenylide is decomposed by *hydrogen sulphide* into mercuric sulphide, benzene, and acetic acid:

$$Hg(C^6H^5)(C^2H^3O^2) + H^2S = HgS + C^6H^6 + C^2H^4O^2;$$

in like manner, but more quickly, by heating in a sealed tube with *ammonium sulphide.*

Mercuric Tolylide. $Hg(C^7H^7)^2$ or $\begin{matrix} C^6H^4 < CH^3 \\ C^6H^4 < CH^3 \end{matrix} > Hg$ (Dreher a. Otto, *loc. cit.*).—Obtained, similarly to the phenyl-compound, by the action of sodium-amalgam on bromotoluene. Beautiful white rhombic tablets, having a nacreous to adamantine lustre, insoluble in water, slightly soluble in cold alcohol, more freely in hot benzol, chloroform, and carbon bisulphide. Melting point 235°. It appears to be analogous in all its reactions to the phenyl-compound. By boiling with *hydrochloric acid* it is resolved into mercuric chloride and toluene, $Hg(C^7H^7)^2 + 2HCl = HgCl^2 + 2C^7H^8$. When carefully heated, it distils almost without decomposition; but on passing its vapour through a red-hot tube filled with pumice, it is resolved into mercury, carbon, toluene, and an oily body, probably ditolyl. Treated with 2 at. *iodine*, *bromine*, or *chlorine*, it is converted into mercuric iodotolylide, $\begin{matrix} C^6H^4—CH^3 \\ Cl \end{matrix} > Hg$, &c.; by 4 at. iodine, &c., into mercuric iodide and iodotoluene, &c.

Mercuric Iodotolylide forms white rhombic tables having a satiny lustre, insoluble in water, slightly soluble in boiling alcohol, more freely in hot benzol; melting at 120°, and subliming without decomposition when cautiously heated.

Mercuric Acetoxytolylide, $Hg(C^7H^7)(C^2H^3O^2)$, prepared like the phenyl-compound, forms small, white, shining, rhombic prisms, melting at 153°, nearly insoluble in cold water, sparingly soluble in boiling water, more easily in alcohol, carbon bisulphide, and benzol. With acids, hydrogen sulphide, and iodine, it reacts like the phenyl-compound.

Mercuric Benzylide, isomeric with mercuric tolylide, and represented by the formula $\begin{matrix} C^6H^5.CH^2 \\ C^6H^5.CH^2 \end{matrix} > Hg$, is not produced by the action of sodium-amalgam either on benzyl bromide or on benzyl chloride. A compound, $Hg(C^7H^7)^2$, called by this name, was described in 1865 by Campisi (*Compt. rend.* lxi. 86) as crystallising in white needles, melting above 200°, soluble in ether, and slightly soluble in alcohol; but its mode of formation is not given.

MESACONIC ACID. $C^5H^6O^4$ (iii. 928).—This acid repeatedly heated to 160° with very strong hydrochloric acid is converted into mesamonochloropyrotartaric acid, $C^5H^7ClO^4$. The latter separates in small shining crystals, much more soluble than mesaconic acid, melting at 129°–130°, and decomposed by boiling with water into hydrochloric and mesaconic acids; by bases with formation of crotonic acid (Swarts, *Jahresb.* 1866, p. 407).

MESIDIC ACID. $C^9H^8O^4 = C^7H^6(CO^2H)^2 = C^6H^3(CH^3)(CO^2H)^2$ (Fittig a. von Furtenbach, *Zeitschr. f. Chem.* [2] iv. 1).—An acid intermediate in composition between mesitylenic acid, $C^9H^{10}O^2$, and trimesic acid, $C^9H^6O^6$. It is produced by oxidising mesitylenic acid with chromic acid mixture; perhaps also, together with mesitylenic acid, in the preparation of the latter by the action of dilute nitric acid on mesitylene. It is nearly insoluble in cold water, very slightly soluble in hot water, more easily in alcohol and ether. From boiling water it crystallises in colourless slender needles, from alcohol in indistinct groups of very small crystals. It melts at 287°–288°, and solidifies again at 286°.

Mesidic acid is bibasic. Its *potassium salt*, $C^9H^6O^4K^2$, crystallises from alcohol in shining laminæ very soluble in water. The *silver salt*, $C^9H^6O^4Ag^2$, is nearly insoluble in cold water, and crystallises from boiling water in colourless dendritic groups. The

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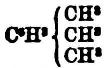
* The equation given in the original memoir for the action of water on acetate of iodine is incorrect.

barium salt, $C^9H^6O^4Ba + H^2O$, is a white cauliflower-like crystalline mass, easily soluble in water. The *calcium salt*, $C^9H^6O^4Ca + H^2O$, forms small, colourless, silvery crystals, less soluble than the barium salt. The neutral solution of the ammonium salt forms with cupric sulphate, lead nitrate, ferric chloride, and zinc sulphate, bulky precipitates slightly soluble in cold water; no precipitate with nickel salts. *Ethyl mesidate*, $C^9H^6O^4.(C^2H^5)^2$, is a colourless radio-crystalline mass, insoluble in water, soluble in all proportions in alcohol, melting at 35°, and having a great tendency to remain liquid.

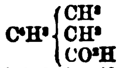
Mesidic acid is identical with uvitic acid produced by the action of baryta-water on pyroracemic acid (v. 971). The same acid is formed by heating the potassium salt of chlorotoluene-sulphuric acid with potassium cyanide, whereby toluylene cyanide, $C^7H^6(CN)^2$, is obtained, and distilling this compound with potash: $C^7H^6(CN)^2 + 3H^2O = 2NH^3 + C^7H^6(CO^2H)^2$ (Irelan, *Zeitschr. f. Chem.* [2] v. 612). Heated with soda-lime it yields toluene: $C^9H^8O^4 = 2CO^2 + C^7H^8$ (Baeyer, *ibid.* iv. 119). By prolonged oxidation with chromic acid it is converted into trimesic acid.

The relations of this acid to mesitylenic and trimesic acids are indicated by the following formulæ:



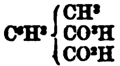
$$C^6H^3\left\{\begin{matrix}CH^3\\CH^3\\CH^3\end{matrix}\right.$$

Mesitylene.



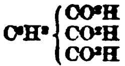
$$C^6H^3\left\{\begin{matrix}CH^3\\CH^3\\CO^2H\end{matrix}\right.$$

Mesitylenic acid.



$$C^6H^3\left\{\begin{matrix}CH^3\\CO^2H\\CO^2H\end{matrix}\right.$$

Mesidic acid.



$$C^6H^3\left\{\begin{matrix}CO^2H\\CO^2H\\CO^2H\end{matrix}\right.$$

Trimesic acid.

MESIDINE or **AMIDOMESITYLENE.** See MESITYLENE, under BENZENE, HOMOLOGUES OF (p. 300).

MESITIC COMPOUNDS (Baeyer, *Ann. Ch. Pharm.* cxl. 297; *Jahresb.* 1866, p. 308).—When acetone saturated with hydrochloric acid gas is left to itself for 8 to 14 days, and then mixed with a large quantity of water, a heavy brownish oil separates consisting chiefly of hydrochlorides of mesityl oxide and phorone. On decomposing this oil with alcoholic potash in a cooled vessel, and subjecting the non-chlorinated oil precipitated by water to fractional distillation, the portion which boils at 140° yields, after washing with water, drying with calcium chloride, and rectification, pure mesityl oxide, $C^6H^{10}O$ (iii. 929), as a colourless liquid smelling strongly of peppermint and boiling at 130°. On carefully mixing it with phosphorus pentachloride till the latter is dissolved, and then pouring the gently warmed liquid into a large quantity of water, the chloride $C^6H^{10}Cl^2$ separates as a heavy oil not volatile without decomposition. This chloride smells strongly like turpentine oil, resinises on exposure to the air, and is decomposed by alcoholic potash-solution, with formation of various products. By distillation over potash, baryta, or lime, it yields the chloride C^6H^9Cl as a mobile colourless liquid having an odour of turpentine, and boiling at 130°.

Nitric acid acts violently on mesityl oxide, forming a yellow resin and an oil smelling like nitrous ether. When mesityl oxide diluted with several times its volume of alcohol is treated with sodium-amalgam, the odour of peppermint disappears, and water then separates from the liquid a colourless oil which smells like camphor and decomposes at about 150°, yielding, together with water, a liquid smelling like camphor, boiling at about 206°, and having the composition of mesitic ether, $C^{12}H^{22}O = (C^6H^{11})^2O$.* The oil produced from mesityl oxide by the action of sodium-amalgam, is regarded by Baeyer as mesitic alcohol, $C^6H^{12}O$ or $C^6H^{11}OH$, which is converted by distillation into the ether: $2C^6H^{12}O = C^{12}H^{22}O + H^2O$. By simple distillation, or more easily by distillation with lime, mesitic ether is decomposed, with formation of higher condensation-products; by distillation with zinc chloride, hydrocarbons are obtained which have not yet been examined.

MESITYLENE. C^9H^{12}.—See BENZENE, HOMOLOGUES OF (p. 298).

MESITYLENE-SULPHURIC or **SULPHOMESITYLIC ACID** (p. 300).

MESITYLENIC ACID. $C^9H^{10}O^2 = C^6H^3\left\{\begin{matrix}CH^3\\CH^3\\COOH\end{matrix}\right.$ (Fittig, *Ann. Ch. Pharm.* cxli. 129; *Jahresb.* 1866, p. 610. Fittig a. Brückner, *Zeitschr. f. Chem.* [2] iv. 493; *Jahresb.* 1867, p. 705. Fittig a. Hoogewerff, *Zeitschr. f. Chem.* [2] v. 169).—An acid isomeric with xylic acid, and related to mesitylene in the same manner as benzoic acid to toluene. It is produced by boiling mesitylene with dilute nitric acid (1 vol. nitric acid of sp. gr. 1·4 and 2 vol. water) for 16 to 20 hours, and passes over with the watery vapours. After complete oxidation, the liquid diluted with a large quantity of water is repeatedly distilled as long as crystals collect in the condensing tube and the acid suspended in the distillate is collected on a filter. The portion which still remains dissolved is obtained by neutralising the filtrate with sodium carbonate, evaporating, and decomposing with hydrochloric acid. For complete purification, the product is boiled with a small quantity of tin and strong hydrochloric acid (to decompose a nitro-compound); and the portion which remains undissolved on cooling is dissolved in sodium carbonate, precipitated at the boiling heat by hydrochloric acid, and crystallised from alcohol. The formation of mesitylenic acid is represented by the equation: $C^9H^{12} + O^3 = C^9H^{10}O^2 + H^2O$.

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* Formerly called mesitic camphor by Baeyer (*Zeitschr. f. Chem.* [2] i. 313). Altogether there is great confusion in the names of these compounds.

Mesitylenic acid dissolves very sparingly in water, very easily in alcohol, and crystallises from the latter in large well-defined monoclinic crystals. When the hot dilute alcoholic solution is mixed with boiling water till permanent turbidity is produced, the acid crystallises in broad laminæ and needles, very much like benzoic acid. It melts at 166°, and sublimes without decomposition even below its melting point. By boiling with chromic acid mixture it is oxidised to trimesic acid:

$$C^9H^{10}O^2 + O^6 = C^9H^6O^6 + 2H^2O.$$

Heated with quick lime it is resolved into carbon dioxide and isoxylene:

$$C^9H^{10}O^2 = CO^2 + C^8H^{10}.$$

Mesitylenic acid is monobasic. All its salts are more or less soluble in water. The *sodium salt*, $C^9H^9O^2Na$, is easily soluble in water and alcohol, and remains on evaporation as a white non-crystalline mass, or as a gradually crystallising syrup. The *silver salt*, $C^9H^9O^2Ag$, is formed in a somewhat concentrated solution, as a precipitate consisting of small needles which may be recrystallised from hot water. The *calcium salt*, $2(C^9H^9O^2)^2Ca + H^2O$, forms crystalline crusts not more soluble in hot than in cold water. The *barium salt*, $(C^9H^9O^2)^2Ba$, forms silky prisms more soluble than the calcium salt. The *magnesium salt*, $(C^9H^9O^2)^2Mg + 5H^2O$, crystallises in groups of monoclinic prisms not much more soluble in hot than in cold water, easily soluble in alcohol, insoluble in ether. The *zinc salt*, $(C^9H^9O^2)^2Zn$, crystallises in laminæ or small needles sparingly soluble in water; the *nickel salt*, $(C^9H^9O^2)^2Ni$, in light green sparingly soluble crusts; the *manganese salt*, $(C^9H^9O^2)^2Mn$, in flesh-coloured scales. The *ethylic ether*, $C^9H^9O^2.C^2H^5$, is a colourless liquid heavier than water, insoluble therein, easily soluble in alcohol, smelling like oil of roses; it boils at 241°, and solidifies in the crystalline form when cooled below 0°.

Chloromesitylenic acid, $C^9H^9ClO^2$, produced by boiling chloromesitylene with dilute nitric acid, is but slightly soluble in water even at the boiling heat, easily soluble in alcohol. Heated above 200°, it turns brown without melting, and may be sublimed without decomposition. The *barium salt*, $(C^9H^8ClO^2)^2Ba + 4H^2O$, crystallises in hemispherical groups of slender colourless needles slightly soluble in cold water. The *calcium salt*, $(C^9H^8ClO^2)Ca + 5H^2O$, forms tufts or fan-shaped groups of flattened needles moderately soluble in hot water (Fittig a. Hoogewerff).

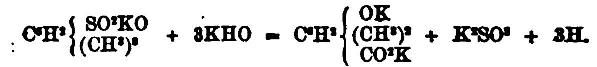
Nitromesitylenic acid, $C^9H^9(NO^2)O^2$, is formed by dissolving mesitylenic acid in fuming nitric acid, and occurs as a secondary product in the distillation-residue of the preparation of mesitylenic acid; it may be purified by precipitation from the sodium or barium salt with hydrochloric acid, and recrystallisation from alcohol. It is very sparingly soluble even in hot water, but dissolves easily in alcohol, and separates from the latter in large crystals, mostly having the aspect of rhombohedral tables; from a solution diluted with hot water, in broad laminæ. It melts at 218°, and sublimes even below that temperature in long needles.

Sodium Nitromesitylenate, $C^9H^8(NO^2)O^2Na$, is deliquescent, and crystallises from alcohol in indistinct prisms. The silver salt, $C^9H^8(NO^2)O^2Ag$, is a flocculent precipitate slightly soluble in boiling water, and separates therefrom in needles. The *barium salt*, $[C^9H^8(NO^2)O^2]^2Ba$, crystallises by slow evaporation from the cold solution in large hard needles containing 3 mol. water; from hot-saturated solution, as a yellow crystalline powder containing 1 mol. water. The *calcium salt*, $[C^9H^8(NO^2)O^2]^2Ca$, is also sparingly soluble, and resembles the mesitylenate in nearly all its properties. The *magnesium salt*, $[C^9H^8(NO^2)O^2]^2Mg + 11H^2O$, forms indistinct prisms insoluble in ether, very soluble in alcohol, moderately soluble in water. The *ethylic ether*, $C^9H^8(NO^2)O^2.C^2H^5$, is insoluble in water, and crystallises from alcohol in short prisms melting at 72°.

Amidomesitylenic acid, $C^9H^9(NH^2)O^2$, produced by heating nitromesitylenic acid with tin and concentrated hydrochloric acid, is sparingly soluble in water, easily in hot alcohol, also in acids and in alkalis; crystallises in long needles, melts at 235°, and decomposes at a higher temperature. It unites with hydrochloric acid, forming the compound $C^9H^9(NH^2)O^2.HCl$, which crystallises from excess of hydrochloric acid in long needles, and is decomposed by heating its aqueous solution, with separation of free amidomesitylenic acid.

Mesitylenamide, $C^9H^9O.NH^2$, is obtained by gently heating 1 mol. mesitylenic acid with rather more than 1 mol. phosphorus pentachloride, adding the product to strong aqueous ammonia, washing the resulting crystalline pulp with dilute ammonia, and recrystallising from boiling water. It crystallises in long needles; melts at 133°; sublimes without decomposition; dissolves sparingly in cold, more easily in boiling water, also in alcohol and ether; and is decomposed by alkalis into ammonia and mesitylenate.

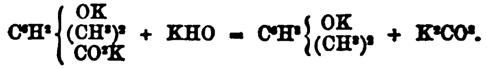
Oxymesitylenic acid, $C^9H^{10}O^3 = C^6H^2\left\{\begin{matrix}OH\\(CH^3)^2\\CO^2H\end{matrix}\right.$, is produced by heating the dry potassium salt of mesitylene-sulphuric acid with three times its weight of potassium hydrate to 240°–250°:



$$C^6H^3\left\{\begin{matrix}SO^2KO\\(CH^3)^2\end{matrix}\right. + 3KHO = C^6H^2\left\{\begin{matrix}OK\\(CH^3)^2\\CO^2K\end{matrix}\right. + K^2SO^3 + 3H.$$

Potassium mesitylene-sulphate. Dipotassic Oxymesitylenate.

Part of the oxymesitylenate is at the same time converted into the potassium-compound of isoxylylic phenol, $C^6H^4(CH^3)^2O$, which is moreover the chief product obtained when the temperature is raised to 280°:



$$C^6H^2\left\{\begin{matrix}OK\\(CH^3)^2\\CO^2K\end{matrix}\right. + KHO = C^6H^3\left\{\begin{matrix}OK\\(CH^3)^2\end{matrix}\right. + K^2CO^3.$$

On dissolving the cooled mass in water, acidulating with sulphuric acid, and distilling, a small quantity of isoxylylic phenol passes over at first with the vapour of water; and if the distillation be continued as long as suddenly solidifying oil-drops appear in the condensing tube, the residual liquid repeatedly agitated with ether, and the ether evaporated, oxymesitylenic acid is obtained as a dark-coloured crystalline mass. It may be purified by repeated solution in sodium carbonate, precipitation with hydrochloric acid, conversion into barium salt, repeated crystallisation of this salt from water, separation of the acid therefrom by hydrochloric acid, repeated crystallisation from alcohol, and final sublimation.

Oxymesitylenic acid melts at 176°; sublimes without decomposition in broad dazzling white needles nearly an inch long, insoluble in cold, slightly soluble in hot water, very soluble in alcohol and ether; and crystallises from dilute alcohol in long silky needles. The aqueous solution of the acid or its salts acquires, on addition of a drop of ferric chloride, a very deep blue colour with a faint tinge of violet, changing to dirty yellow at the boiling heat. Free acids and alkalis interfere with this reaction. *Barium oxymesitylenate*, $(C^9H^9O^3)^2Ba + 5H^2O$, forms compact groups of hard shining laminæ, very soluble in hot, moderately soluble in cold water, turning brown at 110° and black at 130°. The *calcium salt*, $(C^9H^9O^3)^2Ca + 5H^2O$, crystallises in dense tufts of colourless needles easily soluble in water, especially at the boiling heat, somewhat more permanent than the barium salt (Fittig a. Hoogewerff).

MESOSIDERITE. This name is applied by G. Rose to meteorites consisting of nearly equal portions of metal and silicates (*Beschreibung und Eintheilung der Meteoriten*, Berlin, 1864; *Jahresb.* 1863, p. 909; 1865, p. 945).

MESOXALIC ACID. $C^3H^2O^5$.—This acid, originally obtained, together with urea, by boiling alloxan or alloxanic acid with alkalis (iii. 932), is also produced by oxidation of amidomalonic acid, *e.g.* by treating that acid with iodine and water (iv. 115):

$$C^3H^3(NH^2)O^4 + H^2O + I^2 = C^3H^2O^5 + HI + NH^4I.$$

On the preparation of mesoxalic acid from alloxan, see Deichsel (*Berl. Akad. Ber.* 1864, p. 587; *Jahresb.* 1864, p. 640). It crystallises from a syrupy solution evaporated at 40°–50°, and finally over sulphuric acid, in prismatic crystals, $C^3H^2O^5.H^2O$, very deliquescent, easily soluble in alcohol, melting without loss of water at 115°, and resolidifying at 55°. It has a strong acid taste and reaction; decomposes in concentrated aqueous solution at 70°–80°; forms with barium and lead acetate, flocculent precipitates which gradually become crystalline; and after neutralisation with ammonia, is precipitated by barium and calcium salts, also by silver nitrate and mercurous nitrate. The following mesoxalates have been examined by Deichsel:

Ammonium salt .	$C^3O^5(NH^4)^2$,	granular crystals, turning red in the air.
Sodium salt .	$C^3O^5Na^2 + H^2O$,	thin laminæ easily soluble in water.
Silver salt . .	$C^3O^5Ag^2 + H^2O$,	amorphous yellowish precipitate composed of microscopic needles.
Barium salt .	$2C^3O^5Ba + 3H^2O$,	microscopic crystals, nearly insoluble in cold, slightly soluble in hot water, becoming anhydrous at 170°–180°.
Lead salt . .	$C^3O^5Pb.PbH^2O^2$,	nearly insoluble in water.

Ethylic Mesoxalate, $C^3O^5.(C^2H^5)^2 + H^2O$ (?), is formed by treating the silver salt with ethyl iodide and alcohol, as a yellowish non-volatile oil, dissolving easily in water, with formation of mesoxalic acid. With ammonia it forms a crystallisable amide which turns red on exposure to the air.

Mesoxalic acid in dilute aqueous solution treated with *sodium-amalgam*, finally at 80°–90° is converted into tartronic acid, $C^3H^4O^5$. The silver salt boiled with water is resolved into carbonic acid, oxalic acid, and metallic silver, a reaction which may serve for the detection of mesoxalic acid (Deichsel).

On the relations of mesoxalic acid to uric acid and its derivatives, see Uric Acid (v. 958).

METABRUSHITE. A calcic orthophosphate, $PO^4CaH + \frac{3}{2}H^2O$, occurring in monoclinic crystals in the guano of Sombrero (Julien, *Sill. Am. J.* [2] xl. 367; *Jahresb.* 1865, 909).

METACOPAIVIC ACID. See Copaiba (p. 490).

METAHÆMOGLOBIN. A compound of an albuminous substance with a brown colouring matter, produced by the decomposition of hæmoglobin when a concentrated solution of that substance is left to itself at ordinary temperatures, or evaporated to dryness at a temperature above 100°. The brown colouring matter resembles hæmatin in its optical characters, but differs from it in its solubility in water and in dilute acids. The albuminous substance resembles serum albumin (Hoppe-Seyler, *Zeitschr. f. Chem.* 1865, 218; *Jahresb.* 1865, 668).

METAPECTIC ACID. This acid, prepared from mangold-wurzel, is described by C. Scheibler (*Zeitschr. f. Chem.* [2] iv. 433).

METASILICIC ACID. See Silica.

METHACRYLIC ACID. $C^4H^6O^2$ (Frankland a. Duppa, *Chem. Soc. J.* [2] iii. 133).—An acid isomeric with crotonic acid, obtained in the form of an ethylic ether by the action of phosphorus trichloride on ethylic dimethoxalate: $C^4H^8O^3 - H^2O = C^4H^6O^2$. (See Acids, Organic, p. 41; also iv. 273.) By boiling the ether thus produced with alcoholic potash, and distilling the resulting potassium salt with sulphuric acid, methacrylic acid is obtained as a colourless oil, not solidifying at 0°, having a faint odour of pyrogallic acid, and a strong acid reaction. Its salts exhibit the same tendency as those of the other acids of the acrylic series to give up their acid on evaporation. The silver salt is a white precipitate not much affected by light. The barium salt is gummy, very easily soluble; the copper salt moderately soluble in water.

Methacrylic acid heated with potash to the temperature of boiling oil is resolved into propionic and formic acids:

$$C^4H^6O^2 + 2H^2O = C^3H^6O^2 + CH^2O^2 + H^2,$$

differing therein from crotonic acid, which yields only acetic acid.

METHANE. CH^4. *Marsh Gas. Methyl Hydride.*—This gas is decomposed by the continued passage of electric sparks, partly into hydrogen and carbon, partly into hydrogen and acetylene: $2CH^4 = C^2H^2 + 3H^2$. The volume of gas obtained is, however, less than the calculated quantity, because part of the acetylene is converted into liquid polymerides (Berthelot, *Compt. rend.* lxvii. 1188; *Zeitschr. f. Chem.* [2] v. 150).

Dimethyl-dichoromethane. $C^3H^6Cl^2 = C\left\{\begin{matrix}CH^3\\ Cl^2\\ CH^3\end{matrix}\right.$.—This compound, isomeric with propylene chloride, and likewise called *methyl-chloracetol* (iii. 1003), is produced by the action of phosphorus pentachloride on acetone (iii. 1003):

$$C\left\{\begin{matrix}CH^3\\ O\\ CH^3\end{matrix}\right. + PCl^3Cl^2 = PCl^3O + C\left\{\begin{matrix}CH^3\\ Cl^2\\ CH^3.\end{matrix}\right.$$

Friedel a. Ladenburg (*Ann. Ch. Pharm.* cxlii. 310) prepare it by dropping acetone upon phosphorus pentachloride, cooling the mixture at first, and afterwards distilling it, till the liquid which passes over dissolves in water without leaving any oily residue. The distillate washed with water and dried yields by repeated rectification chloropropylene, C^3H^5Cl, between 25° and 35°, and dimethyl-dichloromethane between 66° and 78°.

Dimethyl-diethyl-methane or *Carbodimethyl-diethyl.* $C^7H^{16} = C\left\{\begin{matrix}(C\,H^3)^2\\(C^2H^5)^2\end{matrix}\right.$.—This hydrocarbon, isomeric with heptane or septane, is produced by gently heating dimethyl-dichloromethane with zinc-ethyl. The two bodies do not act on one another in the cold, and if they are heated together in sealed tubes, explosion takes place; but if the dimethyl-dichloromethane be added by drops to zinc-methyl contained in a flask with an upright condenser, the mixture gently heated for some time, and then distilled, dimethyl-diethyl-methane will be found in the portion boiling below 110°. This distillate must be mixed with water, added by drops in a cooled flask, to decompose unaltered zinc-ethyl, the resulting zinc oxide dissolved in hydrochloric acid, and the residual oil submitted after drying to fractional distillation. The portion which then distils between 85° and 90° yields, after being heated for several days with sodium (to remove chlorine), pure dimethyl-diethyl-methane, boiling between 86° and 87°, having a vapour-density = 3·46 (obs. 3·62), and a sp. gr. of 0·7111 at 0°; 0·6958 at 20·5°.

Dimethyl-chloriodomethane or *Methyl-iodochloracetol*, $C\left\{\begin{matrix}CH^3\\CII\\CH^3\end{matrix}\right.$, is produced by heating chloropropylene, C^3H^5Cl, with concentrated hydriodic acid. It is a liquid boiling between 110° and 130°. Treated with silver benzoate it is converted into *dimethyl-dioxybenzomethane* or *methyl-benzacetol*, $C\left\{\begin{matrix}(C\,H^3)^2\\(C^7H^5O^2)^2\end{matrix}\right.$, isomeric with propylene dibenzoate. This compound crystallises from ether in oblique rectangular octohedrons, and is decomposed by water into benzoic acid and a liquid smelling like acetone (Oppenheim, *Bull. Soc. Chim.* x. 128).

METHENYL. CH'''.—The triatomic radicle derived from methane by abstraction of 3 at. hydrogen; it may be supposed to exist in chloroform, $CHCl^3$, iodoform, CHI^3, &c.

METHENYL-SULPHUROUS ACID. $CH^4S^3O^9 = (CH)'''.(SO^3H)^3$. *Methintrisulphonic acid* (Theilkuhl, *Ann. Ch. Pharm.* cxlvii. 134; *Chem. Soc. J.* [2] vi. 192).—This acid, the third term of the series of which methyl-sulphurous acid, $CH^3.SO^3H$, and methylene-sulphurous acid, $CH^2.(SO^3H)^2$, are the two preceding terms, is produced as a calcium salt by heating well-dried calcium methylsulphate on the water-bath for a day, with six times its weight of strongly fuming sulphuric acid containing about 10 p. c. of the anhydride. The product may be purified by boiling with water to decompose unaltered methyl-sulphuric acid, neutralising with lime, precipitating the excess of lime from the filtrate by carbonic acid, and recrystallising. The *calcium salt*, $(CHS^3O^9)^2Ca^3 + 12H^2O$, thus obtained separates in very fine crystals from a moderately concentrated aqueous solution covered with a layer of alcohol and left to itself for several days. It gives off 10 mol. water at 120°, the remaining 2 mols. at 180°, and is not easily decomposed by high temperature or by oxidising agents. The *barium salt*, $(CHS^3O^9)^2Ba^3 + 9H^2O$, separates in shining laminæ on mixing the calcium salt with barium chloride, and crystallises from boiling water or boiling dilute sulphuric acid in beautiful needles or laminæ; gives off 6 mol. water at 100° and the rest at 200°. A *basic lead salt*, $(CHS^3O^9)^2Pb^3.2PbO$, is precipitated by lead acetate from a warm solution of the calcium salt containing a little alcohol, in stellate groups of needles sparingly soluble in water. The *potassium salt*, $CHS^3O^9K^3 + H^2O$, obtained by exactly precipitating a boiling solution of the calcium salt with potassium bicarbonate, is easily soluble in water, and crystallises in small shining prisms, which give off their water at 100°. The *free acid*, or *hydrogen salt*, obtained by decomposing the lead salt with hydrogen sulphide, and carefully evaporating in a vacuum over sulphuric acid, forms long, very deliquescent needles, having a strong acid reaction, easily soluble in absolute alcohol, and separating therefrom in needles.

METHINTRISULPHONIC ACID. See the last article.

METHYL. $(CH^3)^2$.—See ETHANE.

METHYL-ACETONE. Syn. with METHYL-ETHYL KETONE (p. 766).

METHYL ALCOHOL and **ETHERS.** Methyl alcohol, CH^3OH, may be prepared from hydrocyanic acid by converting that compound into methylamine by Mendius's process (iv. 58), and boiling the slightly acid aqueous solution of the nitrite of that base, whereby it is resolved into methyl alcohol, water, and nitrogen:

$$CH^5N.HNO^2 = CH^4O + H^2O + N^2.$$

The methyl alcohol thus obtained boils at 66°–66·5° (corr. 67·1°), and has a sp. gr. of 0·8574 at 21° (Linnemann, *Zeitschr. f. Chem.* [2] iv. 284).

Methyl Bromide is produced by boiling amyl bromide with methyl alcohol: $C^5H^{11}Br + CH^3OH = C^5H^{11}OH + CH^3Br$ (Hofmann a. Girard, *Zeitschr. f. Chem.* [2] v. 653).

Methyl Chloride, exposed to the action of chlorine in direct sunshine is converted mainly into dichlorinated methyl chloride or methylene dichloride, CH^2Cl^2. By washing the gaseous product with water, passing it into glacial acetic acid, which absorbs it, then slowly heating the saturated acetic acid to 100°–105°, and mixing the distillate with water, an oil is obtained which begins to boil at 30°, the temperature, however, quickly rising to 40°, and about half of the product passing over between 40° and 50°. This distillate after two rectifications yielded a liquid boiling at 40°–42°, and having the composition CH^2Cl^2. The products of higher boiling point consisted of chloroform and carbon tetrachloride (Perkin, *Chem. Soc. J.* [2] vii. 260).

Methyl Sulphoxide. $(CH^3)^2SO$ (Saytzeff, *Ann. Ch. Pharm.* cxliv. 148; *Jahresb.* 1867, p. 540).—Methyl sulphide added by drops to cooled fuming nitric acid dissolves to a homogeneous liquid which when evaporated leaves the *nitrate of methyl sulphoxide*, $(CH^3)^2SO.HNO^3$, which after pressure, standing over lime, and recrystallisation from water, forms colourless deliquescent needles dissolving very easily in water, with acid reaction, less easily in alcohol and ether, melting at 100°, and decomposing with slight explosion at a higher temperature. When its aqueous solution is treated with barium carbonate, and the evaporated residue is digested with absolute alcohol, methyl sulphoxide, $(CH^3)^2SO$, dissolves, and remains, after evaporation of the alcohol, as a colourless, inodorous, syrupy liquid, which solidifies to a crystalline mass on cooling. It is not volatile without decomposition, dissolves easily in water, alcohol, and ether, and is reduced by zinc and sulphuric acid to methyl sulphide.

When methyl sulphoxide is heated to 100° for five or six hours with concentrated sulphuric acid, a solution is formed, which on evaporation leaves methylsulphone, $(CH^3)^2SO^2$, as a viscid mass which crystallises on cooling. This compound dissolves easily in water, alcohol, and fuming nitric acid, crystallises therefrom in prisms, sublimes at 100°, boils without decomposition at 238°, melts at 109°, and solidifies again at 99°. By zinc and dilute sulphuric acid it is also reduced to methyl sulphide.

Methyl Bisulphoxide, $(CH^3)^2S^2O^2$, is produced by treating the bisulphide, $(CH^3)^2S^2$, with nitric acid of sp. gr. 1·2 diluted with an equal volume of water. After washing with water and drying with calcium chloride, it forms a colourless oil heavier than water. It is converted into methyl-sulphuric acid by strong nitric acid, and reduced to methyl bisulphide by zinc and dilute sulphuric acid (Saytzeff, *Zeitschr. f. Chem.* [2] iv. 641).

The trimethyl-sulphurous compounds produced by combination of methyl sulphide, $(CH^3)^2S$, with ethyl iodide, bromide, &c., are described in vol. v. p. 885.

METHYL-ALLYL. $CH^3.C^3H^5$.—This hydrocarbon, identical or isomeric with butylene, is produced by heating a mixture of zinc-methyl and allyl iodide with sodium to 120°, or by heating a mixture of methyl and allyl iodides with sodium to 100° (p. 375).

METHYLAMINE. $CH^3.H^2N$.—When an aqueous solution of this base is set on fire, the hydrogen chiefly burns, and hydrocyanic acid is found in the remaining liquid: $CH^5N + O^2 = CHN + 2H^2O$ (Tollens, *Zeitschr. f. Chem.* [2] ii. 516). Methylamine heated with saturated hydriodic acid yields ammonia and methane: $CH^5N + 2HI = CH^4 + NH^3 + I^2$ (Berthelot).

Trimethylamine is said to occur in *Arnica montana* (Hesse, *Jahresb.* 1864, p. 458), in the seeds of the beech (Brandl a. Rakowiecki, *ibid.* 607), and in *Cotyledon umbilicus*. According to E. Ludwig (*Zeitschr. f. Chem.* iv. 96), it occurs in small quantity in several Austrian and Hungarian wines.

Trimethyl-oxethylammonium Hydrate.– See CHOLINE (p. 448).

METHYL-AMYL-ACETONE. Syn. with methyl-hexyl ketone, $CO\left\{\begin{matrix}CH^3\\C^6H^{13}\end{matrix}\right.$ $= CO\left\{\begin{matrix}CH^3\\CH^2(C^5H^{11})\end{matrix}\right.$. (See KETONES, p. 766.)

METHYL-BENZACETOL. See page 826.

METHYL-BENZENES. Several methylic derivatives of benzene have already been described, viz. monomethyl-benzene or toluene, $C^6H^5.CH^3$ (p. 279), dimethyl-benzene, $C^6H^4(CH^3)^2$, and trimethyl-benzene, $C^6H^3(CH^3)^3$, the last two occurring in several modifications (pp. 293, 296, 298).

Tetramethyl-benzene or **Durene,** $C^{10}H^{14} = C^6H^2(CH^3)^4$, isomeric with cymene (p. 302), has lately been obtained by Jannasch a. Fittig (*Zeitschr. f. Chem.* [2] vi. 161). It is prepared by the action of sodium and methyl-iodide on monobromo-pseudocumene in ethereal solution:

$$C^6H^2Br(CH^3)^3 + CH^3I + Na^2 = NaI + NaBr + C^6H^2(CH^3)^4.$$

After six days' digestion, the liquid was distilled and the product fractionated. After the first distillation, the whole of the liquid collected between 170° and 200° solidified in the crystalline form on cooling, the last portion completely. After two or three distillations, the greater portion passed over between 185° and 195°, and solidified completely on cooling. It was purified by repeated pressure between paper, drying over sulphuric acid, and rectification.

Durene is the only known hydrocarbon of the benzene series which is solid at ordinary temperatures. It dissolves easily in alcohol, ether, and benzene; crystallises from alcohol in compact crystals belonging either to the monoclinic or to the triclinic system; has but a faint benzolic odour; melts between 79° and 80°; and boils constantly at 189°–191°. It floats on water, volatilises with aqueous vapour, and burns with a very bright flame.

Dibromodurene, $C^{10}H^{12}Br^2 = C^6Br^2(CH^3)^4$, is formed, with violent reaction, when durene is dissolved at ordinary temperatures in excess of bromine; the product may be purified by washing with soda-ley and with water. It is nearly insoluble in cold alcohol, but slightly soluble in boiling alcohol, and crystallises therefrom in thin silky brittle needles; melts at 199°, and sublimes undecomposed at higher temperatures.

Dinitrodurene, $C^{10}H^{12}(NO^2)^2 = C^6(NO^2)^2(CH^3)^4$, separates as a white precipitate, when durene is added to cold very strong nitric acid, and the resulting solution is poured into water; it crystallises from alcohol in colourless shining rhombic prisms, from benzene in compact crystals. It is easily soluble in ether, somewhat less in benzene, still less in hot alcohol, very slightly in cold alcohol. It melts at 199°, and sublimes without decomposition at a higher temperature in splendid shining needles.

Oxidation-products of Durene (Jannasch, *Zeitschr. f. Chem.* [2] vi. 449; vii. 33).—By oxidising durene with dilute nitric acid, two acids are obtained, one of which volatilises with the aqueous vapour, while the other remains behind.

Cumylic acid, $C^{10}H^{12}O^2 = C^6H^2(CH^3)^3.CO^2H$, the more volatile of these two acids, is the third homologue of benzoic acid. It is nearly insoluble in cold water, very slightly soluble in boiling water, very easily soluble in alcohol and ether, somewhat lese soluble in benzene, from which it crystallises on cooling in irregular arborescent groups of hard, limpid, highly lustrous needles. It volatilises with vapour of water, sublimes in long delicate needles, and melts at 140°–150°. It is monobasic. The *barium salt,* $(C^{10}H^{11}O^2)^2Ba + 7H^2O$, crystallises in transparent tabular prisms efflorescing over sulphuric acid. The *calcium salt,* $(C^{10}H^{11}O^2)^2Ca + 2H^2O$, forms smaller crystals arranged in nodular groups.

Cumidic acid, $C^{10}H^{10}O^4 = C^6H^2(CH^3)^2.(CO^2H)^2$, the less volatile acid above mentioned, is bibasic and homologous with phthalic, uvitic, and xylidic acids. It is nearly insoluble in water, very slightly soluble in ether and in benzene, more readily in boiling alcohol. On adding benzene to the alcoholic solution, the acid slowly crystallises in long transparent needles. At a very high temperature it sublimes, without previous fusion, and condenses in small shining transparent plates. The *barium salt,* $C^{10}H^8O^4Ba + 2H^2O$, forms rhombic plates having a fine pearly lustre. The *calcium salt,* $C^{10}H^8O^4Ca + 2H^2O$, crystallises in small, very shining, transparent, very compact prisms.

METHYL-CHLORACETOL. Syn. with DIMETHYL-DICHLOROMETHANE (p. 825).

METHYL-CROTONIC ACID. $C^5H^8O^2$ (Frankland a. Duppa, *Chem. Soc. J.* [2] iii. 133).—Isomeric with angelic acid. Its ethylic ether, $C^5H^7O^2.C^2H^5$, produced by the action of phosphorus trichloride on ethylic ethomethoxalate (iv. 275), is a mobile liquid having an intolerable odour of decayed fungi, and a burning taste; boiling at 156°; insoluble in water, but miscible in all proportions with alcohol and ether. By alcoholic potash, it is resolved into alcohol and methyl-crotonic acid, which melts at 62°, and crystallises on cooling in shining needles, much more soluble in water than ethyl-crotonic acid (p. 600). Its *barium salt,* $(C^5H^7O^2)^2Ba$, is easily soluble and difficult to crystallise; the *silver salt*, $C^5H^7O^2Ag$, is a white crystalline powder, slightly soluble in water. Methyl-crotonic acid heated with potassium hydrate, is resolved, like angelic acid, into propionic and acetic acids:

$$C^5H^8O^2 + 2H^2O = C^3H^6O^2 + C^2H^4O^2 + H^2.$$

METHYL-DIACETIC ACID. $C^5H^8O^3$ (R. Brandes, *Jenaische Zeitschr.* iii. 25; *Jahresb.* 1866, p. 305). *Formate of Acetylinated Ethyl* (p. 590).—Produced by the action of sodium on methyl acetate, in the same manner as ethyl-diacetic acid from ethyl acetate (p. 601). The sodium salt, which is the direct product of the reaction, may be purified by treatment with anhydrous ether. It is slightly soluble in pure ether, easily in alcoholic ether, and is decomposed gradually by contact with the air, more quickly by boiling its aqueous solution, in the manner represented by the following equation:

$$\underset{\text{Sodium methyl-diacetate.}}{2C^5H^7O^3Na} + 3H^2O = \underset{\text{Acetone.}}{2C^3H^6O} + \underset{\text{Methyl alcohol.}}{2CH^4O} + \underset{\text{Sodium carbonate.}}{CO^3Na^2} + CO^2.$$

Methyl-diacetic acid separated from the sodium salt by acetic acid, and purified by agitation with ether and fractional distillation of the ethereal extract, is a colourless liquid having a fruity odour, a sp. gr. of 1·037, and boiling at 169° to 179°. With ferric chloride it produces a characteristic dark cherry-red colour, rose-red in very dilute solutions. It distils with aqueous vapour in oily drops, and is decomposed by heating with strong acids and bases, in the same manner as the sodium salt by boiling with water. The *copper salt*, $(C^5H^7O^3)^2Cu + 2HO$, separates on adding cupric acetate to the acid neutralised with baryta-water, in pale green crystals insoluble in alcohol. When heated with water it is decomposed like the ethyl-diacetate. The *methylic ether*, $C^5H^7O^3.C^2H^5$, obtained by heating the sodium salt with methyl iodide, is a colourless liquid boiling at 177·4°; having a sp. gr. of 1·020 at 9°; smelling like mint when diluted, and producing a violet-red coloration with ferric chloride. The *ethylic ether*, $C^5H^7O^3.C^2H^5$, prepared in like manner, boils at 189·7° (corr.) and has a sp. gr. of 0·995 at 14°. It is distinguished from the isomeric compound, methylic ethyl-diacetate, by its somewhat lower boiling point, and by producing a splendid violet-red colour with ferric chloride. By prolonged contact with strong aqueous ammonia, it forms an oil, $C^7H^{13}NO^3$, which may be either the amide of ethyl-methyl-diacetic acid, or the ethylamide of methyl-diacetic acid, and a solution which on evaporation yields the amide of methyl-diacetic acid, $C^5H^9NO^2$, in concentric groups of silky needles melting at 82°–83°.

In the rectification of methyl-diacetic acid there remains, together with colouring matter, a crystallisable substance which volatilises with vapour of water and exhibits the composition and properties of dehydracetic acid, $C^8H^8O^4$ (p. 543). The same acid is also formed by heating sodium methyl-diacetate to 170° in dry carbonic acid gas, methyl-diacetic acid then distilling, whilst dehydracetate and carbonate of sodium remain behind, together with a resinous body.

METHYL-DIETHYL-CARBINOL. $C^6H^{14}O = CH^3(C^2H^5)^2.COH$.—See HEXYL ALCOHOLS (p. 698).

METHYLENE-COMPOUNDS. The *chloride*, CH^2Cl^2, is produced: 1. By the action of chlorine on methylene iodide (iii. 1005); to remove the last traces of iodine, prolonged treatment with chlorine at ordinary temperatures is required (Buttlerow, *Zeitschr. f. Chem.* [2] v. 276).—2. By the action of chlorine on methyl chloride in sunshine (Perkin, p. 827).—3. Together with marsh gas, by agitating an alcoholic solution of chloroform with excess of zinc-powder and a small quantity of ammonia. The methylene-chloride thus produced is separated from unaltered chloroform by fractional distillation (Perkin, *Chem. News*, xviii. 106). It is a colourless mobile liquid, smelling like chloroform and having a burning taste; slightly soluble in water, especially at high temperatures. Sp. gr. 1·3604 at 0°; coefficient of expansion for 1° between 0° and + 20° = 0·00137. Boiling point 40° (Buttlerow); 40°–42° (Perkin). The idea formerly entertained of the existence of two isomeric compounds having the composition CH^2Cl^2 is no longer admissible.

Methylene Iodide, CH^2I^2, is produced by heating chloroform with hydriodic acid to 125° in sealed tubes; probably thus: $CHCl^3 + 3HI = 3HCl + CHI^3$; and $CHI^3 + HI = I^2 + CH^2I^2$ (Lieben, p. 438).

Hexamethylenamine. $C^6H^{12}N^4 = (C''H^2)^6N^4$.—A base produced by the action of dry ammonia gas on pulverised oxymethylene (dioxymethylene, iii. 1007):

$$(CH^2O)^6 + 4NH^3 = C^6H^{12}N^4 + 6H^2O;$$

or by heating a mixture of vapour of oxymethylene and ammonia gas to 160°–170°.

It crystallises from alcohol in colourless shining rhombohedrons or short prisms; is inodorous in the cold, but has a very disagreeable odour when heated; sublimes slowly at 100° in small highly lustrous crystals; dissolves easily in water and in boiling alcohol, less easily in cold alcohol, scarcely at all in ether; has a distinct alkaline reaction. The *hydrochloride*, $C^6H^{12}N^4.HCl$, is easily soluble in water, slightly soluble in alcohol; crystallises in long white needles; melts and decomposes completely when heated. Its solution forms with *platinic chloride* a pale orange-coloured precipitate, often exhibiting octohedrons and tetrahedrons, insoluble in cold water, decomposed by boiling water (Buttlerow, *Ann. Ch. Pharm.* cxv. 322; *Zeitschr. f. Chem.* [2] v. 278).

METHYL-HEXYL. $CH^3.C^6H^{13}$.—See HEPTANE (p. 696).

METHYL-HYDANTOÏN. See HYDANTOÏN (p. 703).

METHYLIC ALDEHYDE. See FORMIC ALDEHYDE (p. 622).

METHYL-IODOCHLORACETOL. Syn. with DIMETHYL-CHLORIODOMETHANE (p. 826).

METHYLURAMINE, $C^2H^7N^3$, may be regarded as carbomethyltriamine,

$N^3\left\{\begin{matrix}C^{iv}\\CH^3\\H^4\end{matrix}\right.$ (Hofmann, *Ann. Ch. Pharm.* cxxxix. 107).

MIASCITE. Analyses of this rock from Ditro in Transylvania have been made by Fellner (*Jahresb.* 1867, p. 1026).

MILK-ANALYSIS. According to Wanklyn, whose researches on milk are published in the *Milk Journal*, almost the only sophistications to which milk is actually subjected are the more or less complete removal of the cream, and dilution with water. Out of some hundreds of samples of milk bought in London in the present year (1871), so large a proportion as about $\frac{9}{10}$ were found to have been either skimmed or watered, or both skimmed and watered, no other kind of adulteration being recognised. The method of examination consisted in taking the solid residue dried at 100° and measuring the yield of cream, or else estimating the fat by means of ether.

Contrary to what has been often stated, Wanklyn finds that a milk residue may be easily and conveniently dried until its weight is quite constant at 100° C. For this purpose, about 5 grams of milk are evaporated in the water-bath, in a thin platinum dish, and maintained at 100° for the space of three hours, when the weight of the solid residue will be found to have become constant, being incapable of sensible diminution by prolonging the drying for three hours longer. The following examples may be cited (see *Milk Journal*, vol. i. p. 109). A specimen of genuine country-fed milk furnished in four experiments:

	Milk.		Solids dry at 100°.	Percentage of solids.
I.	4·969 grams	gave	0·616 grams	12·40
II.	5·0105 „	„	0·6255 „	12·48
III.	5·007 „	„	0·623 „	12·44
IV.	5·0145 „	„	0·626 „	12·48
	Mean percentage of solids		. . .	12·45

A specimen of very rich town-fed milk gave in four experiments:

	Milk.		Solids.	Percentage.
I.	5·000 grams	gave	0·7035 grams	14·07
II.	5·004 „	„	0·705 „	14·09
III.	5·000 „	„	0·7025 „	14·05
IV.	5·006 „	„	0·705 „	14·08
	Mean percentage of solids		. . .	14·07

The complete analyses of the two kinds of milk furnished the following results:

	Country milk.	Town milk.
Water	87·55	85·93
Fat	3·07	4·00
Casein	4·04	5·02
Milk-sugar . . .	4·63	4·31
Ash	0·71	0·74
	100·00	100·00

periodate, $2KIO^4.Zn^4I^2O^{11} + 4H^2O$, is precipitated by tetrapotassic periodate from a solution of zinc sulphate; the acid filtrate contains zinc as well as periodic acid, and gradually deposits crystals of normal potassium periodate (Rammelsberg).

Nickel Salts.—Recently precipitated nickel carbonate dissolves in periodic acid, with green colour, and formation of peroxide, iodate, and insoluble basic periodate of nickel. The acid green solution evaporated at a very gentle heat, or over oil of vitriol, yields light green crystals (rectangular four-sided prisms with oblique end-faces) of the salt $Ni^7I^8O^{33}$ or $NiI^2O^6.3Ni^2I^2O^9$, with variable amount of water (49 to 63 mol.). It is insoluble in water, but blackens when heated with water, forming iodate and peroxide of nickel. The same compound is precipitated from the acid mother-liquor by incomplete saturation with ammonia (Rammelsberg).

Cobalt Salts.—Lautsch by treating dry tetrasodic periodate with excess of cobalt sulphate, or by evaporating a solution of the two salts to dryness, obtained a dark yellow-greenish powder, to which he assigns the composition $Co^7I^4O^{21} + 16H^2O$ or $7CoO.2I^2O^7 + 16H^2O$; he finds, however, that it gives off chlorine when dissolved in hydrochloric acid: hence it should contain a cobaltic compound. According to Rammelsberg, alkaline periodates produce in solutions of cobaltous salts a precipitate consisting of hydrated cobalt peroxide mixed with cobaltous iodate (part of the latter also remaining in solution); the same products are likewise formed when cobaltous carbonate is dissolved in periodic acid. Exactly similar results are obtained with manganous salts. Ferrous salts yield with alkaline periodates a brownish-yellow precipitate of ferrous iodate.

Ferric Periodate, $(Fe^4)^{xii}I^2O^{13} + 21H^2O$ or $2Fe^2O^3.I^2O^7 + 21H^2O$, is formed on adding tetrapotassic periodate to solutions of ferric salts, as a light brownish-yellow precipitate, which dries up to dark brown lumps having a shining fracture.

Cadmium Salts.—The normal salt, CdI^2O^8, is formed as a heavy white powder mixed with a small quantity of the following salt, on treating cadmium carbonate with a hot solution of periodic acid. If an insufficient quantity of the acid is used, the tetracadmic salt $Cd^4I^2O^{11} + 3H^2O$ is produced. The acid mother-liquor of these two salts yields by spontaneous evaporation, the salt $Cd^2I^2O^9 + 9H^2O$ in rectangular four-sided tables belonging to the rhombic system. It is insoluble in water, and is converted by boiling therewith into a yellowish powder. A fourth salt, $Cd^{10}I^6O^{31} + 15H^2O$, or perhaps $Cd^2I^2O^9.2Cd^4I^2O^{11} + 15H^2O$, is obtained as an insoluble white precipitate, on pouring cadmium sulphate into normal sodium periodate.

Copper Salts.—The *pentacupric salt*, $Cu^5I^2O^{12} + 5H^2O$, separates as a green powder on adding cupric carbonate to aqueous periodic acid: it gives off half its water at 200°. When a solution of cupric nitrate is mixed with normal potassium periodate, a green precipitate is formed at first, and the blue acid filtrate afterwards deposits the tetracupric salt, $Cu^4I^2O^{11} + 7H^2O$, in dark green microscopic crystals. A solution of recently precipitated cupric hydrate in periodic acid first deposits the pentacupric salt, and then, by spontaneous evaporation, the dicupric salt $Cu^2I^2O^9 + 6H^2O$, in dark green crystalline aggregates. A *potassio-cupric salt* of uncertain composition is formed as a bright green precipitate on mixing the solutions of cupric nitrate and tetrapotassic periodate (Rammelsberg). Lautsch obtained the salt $Cu^4H^2I^2O^{12}$ or $4CuO.I^2O^7 + H^2O$, as a green crystalline mass, by treating the dry sodium salt with aqueous cupric sulphate, or as a siskin-green powder, by mixing the solutions of cupric sulphate and tetrasodic periodate (whereby no precipitate is produced), evaporating to dryness, redissolving, again evaporating, and washing (Rammelsberg).

Lead Salt.—The lead periodate precipitated on mixing the solutions of normal sodium periodate and lead nitrate has the composition $Pb^3I^2O^{10} + 2H^2O$ established by Langlois. When heated with a solution of periodic acid, it acquires a yellowish-red colour without giving up any of its lead, and is afterwards insoluble in nitric acid (Rammelsberg).

Mercury Salts.—A slightly acidulated solution of mercurous nitrate forms with normal sodium periodate a precipitate of *octomercurous periodate*, $Hg^8I^2O^{11}$ or $4Hg^2O.I^2O^7$, having a fine yellow colour. It is anhydrous, soluble in nitric acid, and when heated is resolved without residue into yellow and red mercuric iodide, metallic mercury, and oxygen (Rammelsberg). A *decamercurous salt*, $Hg^{10}I^2O^{12}$ or $5Hg^2O.I^2O^7$, is obtained by precipitating the solution of the tetrasodic salt with mercurous nitrate, or by digesting the same sodium salt in the solid state with the mercurous solution, as a light yellow precipitate, affording a characteristic reaction of periodic acid; it becomes somewhat darker at 100°, dissolves in nitric acid, and likewise in hydrochloric acid, with evolution of iodine chloride. Hydrogen sulphide throws down mercury from these solutions, without previous separation of iodine. Stannous chloride converts the aspect of ferric hydrate, whilst only very small quantities of trioxide remain in solution: hence the dioxide cannot be regarded as a molybdate of the sesquioxide, $Mo^2O^3.MoO^3$. *Blue oxide of molybdenum* is obtained by mixing the brown solution of the dioxide with a solution of the trioxide in hydrochloric acid, and washing the precipitate with a mixture of alcohol and sal-ammoniac. After drying over sulphuric acid it has the composition $Mo^2O^5 + 3H^2O$. By strong bases it is decomposed, like the other blue oxides of molybdenum, into dioxide and trioxide. When a mixture of molybdic chloride and ammonium molybdate is left to itself for some time, crystals form in the blue precipitate, which may be purified by washing with alcohol. They are very small, prismatic, brown by transmitted light, and dissolve in water, forming a yellow solution, with separation of dioxide; silver salts added to this solution throw down a yellow precipitate easily soluble in nitric acid. Heated out of contact with the air, they give off water and ammonia, and leave a blue oxide containing Mo^3O^8. Their composition may be represented by the formula $2(MoO^2.MoO^3).(NH^4)^2O.2MoO^3 + 9H^2O$.

The *dioxide*, MoO^2, is obtained in the crystalline form by fusing sodium molybdate in a porcelain crucible with a third of its weight of zinc added by small portions, the heat being continued till the crystalline growth which spreads out from the zinc fills the entire liquid. The cooled mass digested alternately with caustic potash and hydrochloric acid, and washed with water, leaves the dioxide in dark blue-violet prisms, having a strong metallic lustre, and appearing light violet-red by transmitted light. They conduct electricity well (quickly becoming covered with copper when immersed in solution of cupric sulphate in contact with zinc); are not attacked by hydrochloric acid or potash-ley even at the boiling heat; but are converted into trioxide by heating with nitric acid. Sodium molybdate is not reduced by tin (Ullik, *Jahresb.* 1867, p. 237).

Trioxide or *Molybdic Anhydride.*—On the preparation of this oxide from native lead molybdate, see Ullik (*Zeitschr. f. Chem.* [2] iv. 690). The soluble (colloïdal) modification (iii. 1036) may be prepared by decomposing precipitated barium molybdate with an exactly equivalent quantity of sulphuric acid. The solution evaporated over sulphuric acid leaves soluble molybdic acid in the form of a transparent blue or blue-green mass, easily soluble in water, but gradually becoming less soluble by keeping, and converted at higher temperatures, *with loss of water*, into ordinary molybdic anhydride (Ullik). According to Graham, the colloïdal solution evaporated at 100° leaves *soluble* molybdic anhydride.

Amorphous soluble molybdic acid retains at different temperatures constant quantities of water, corresponding to definite hydrates, $H^2O.2MoO^3$ being formed at 100°, $H^2O.4MoO^3$ at 120°, and $H^2O.8MoO^3$ at 160°–170°. The hydrate $H^2O.2MoO^3$ is also formed when molybdic acid is left for several months over oil of vitriol. The hydrate $H^2O.5MoO^3$ is produced: 1. By evaporating a solution of amorphous molybdic acid over the water-bath.—2. By boiling a solution of the magnesium salt, $MgO.MoO^3 + 7H^2O$, with a large excess of nitric acid.—3. By boiling the aqueous solution of amorphous molybdic acid with sulphuric acid. This hydrate separates as a fine white powder which is nearly insoluble in water, and when suspended therein forms a milky liquid which runs through the filter; it may however be washed by decantation with water containing nitric acid. It does not lose weight over oil of vitriol or at 100°. The hydrate, $H^2O.MoO^3$, was once obtained accidentally when a solution of the salt $MgO.MoO^3 + 7H^2O$ was mixed with a quantity of nitric acid nearly equivalent to the magnesium and left to itself. It formed crystalline crusts composed of very small needles, nearly insoluble in cold, very slightly soluble in hot water, and not losing weight at 100° (Ullik, *Ann. Ch. Pharm.* cliii. 368).

A weak solution of molybdenum trioxide in nitric acid yields with potassium xanthate, even in very dilute solutions, a light yellow to flesh-coloured precipitate, which in a few minutes, especially on agitation, assumes a splendid violet colour. More concentrated solutions immediately yield a nearly black coagulating precipitate, which, after drying in a vacuum, has the composition $(C^3H^5O^2S^2)^2Mo + H^2O$ (Siewert, *Jahresb.* 1864, p. 707).

The dark red coloration produced by boiling an ammoniacal solution of molybdic acid for a short time with a moderate excess of yellow *ammonium sulphide*, appears reddish-yellow in more dilute solutions, and after a while brick-red, depositing salmon-coloured flocks; this reaction is perceptible in a solution containing only 0·8 milligr. molybdic anhydride in a litre. On adding to the reddish-yellow solution potassium sulphocyanate and ether (which produce no alteration), then a strongly acid solution of stannous chloride, and agitating, the ether takes up molybdenum sulphocyanate, and acquires an orange-red colour, changing to carmine-red on exposure to the air.

The brown liquid produced by adding the acid solution of stannous chloride to ammonium molybdate exhibits with potassium sulphocyanate and ether the same reaction, which depends on the formation of molybdenum trichloride and trisulphocyanate, and oxidation of the latter to carmine-coloured tetrasulphocyanate:

$$Mo^2Cl^6 + 6KCyS = 6KCl + Mo^2Cy^6S^6;$$
$$2Mo^2Cy^6S^6 + 4HCl + O^2 = 3MoCy^4S^4 + MoCl^4 + 2H^2O.$$

By means of this reaction a trace of molybdenum has been detected in the vanadiferous brown hæmatite of Haverloh (C. D. Braun, *Zeitschr. anal. Chem.* vi. 86; *Jahresb.* 1867, p. 852).

Molybdates (Delafontaine, *Bull. Soc. Chim.* [2] iv. 257; *Jahresb.* 1865, p. 215. Ullik, *Ann. Ch. Pharm.* cxliv. 204, 320; cliii. 368; *Zeitschr. f. Chem.* [2] iv. 690; vi. 434; *Chem. Centr.* 1867, 977; 1870, 117. *Crystalline forms*: Zepharovich, *Wien. Akad. Ber.* lviii. [2] 111; *Jahresb.* 1868, 221).—Several new classes of these salts have lately been discovered, which, together with those previously known, may be formulated as follows, the symbol R standing for 2 atoms of a monatomic or 1 atom of a diatomic metal:

Monomolybdates .	$RO.MoO^3$	=	$\left.\begin{matrix}MoO^2\\R\end{matrix}\right\}O^2$
Dimolybdates . .	$RO.2MoO^3$	=	$\left.\begin{matrix}2MoO^2\\R\end{matrix}\right\}O^3$
$\frac{7}{3}$ Molybdates . .	$3RO.7MoO^3$	=	$\left.\begin{matrix}7MoO^2\\R^3\end{matrix}\right\}O^{10}$
Trimolybdates . .	$RO.3MoO^3$	=	$\left.\begin{matrix}3MoO^2\\R\end{matrix}\right\}O^4$
Tetramolybdates .	$RO.4MoO^3$	=	$\left.\begin{matrix}4MoO^2\\R\end{matrix}\right\}O^5$
Octomolybdates . .	$RO.8MoO^3$	=	$\left.\begin{matrix}8MoO^2\\R\end{matrix}\right\}O^9$
Decamolybdates .	$RO.10MoO^3$	=	$\left.\begin{matrix}10MoO^2\\R\end{matrix}\right\}O^{11}$
Hexdecamolybdates .	$RO.16MoO^3$	=	$\left.\begin{matrix}16MoO^2\\R\end{matrix}\right\}O^{17}$

Monomolybdates or *Neutral Molybdates.* $RO.MoO^3 + nH^2O$.—The solutions of these salts are not coloured by potassium ferrocyanide. The *potassium salt*, first obtained by Svanberg a. Struve (i. 1140), may be prepared by fusing equivalent quantities of potassium carbonate and molybdic anhydride, dissolving the fused mass in hot water, and evaporating the filtered solution over sulphuric acid; it crystallises in anhydrous microscopic prisms (Ullik). Delafontaine, by leaving the solution to evaporate spontaneously, obtained a pentahydrated salt, $K^2O.MoO^3 + 5H^2O$, in transparent hexagonal prisms combined with the end-face and a subordinate hexagonal pyramid. The crystals give off their water at 100°, and melt without decomposition at a red heat. The *sodium salt*, $Na^2O.MoO^3 + 2H^2O$, forms nacreous laminæ or monoclinic tables apparently isomorphous with the corresponding tungstate. A *sodio-potassic salt*, $K^2O.2Na^2O.3MoO^3 + 14H^2O$, is obtained by saturating potassium trimolybdate with sodium carbonate, and leaving the solution to evaporate; it crystallises in hexagonal prisms like those of the pentahydrated potassium salt, easily soluble in hot water, and forming an alkaline solution (Ullik). A *lithium salt*, $5(Li^2O.MoO^3) + 2H^2O$, is obtained, by heating molybdic anhydride with lithium carbonate and water and evaporating, in nodular groups of easily soluble crystals (Rammelsberg, *Jahresb.* 1866, p. 234. Delafontaine). Another salt, containing $3(Li^2O.MoO^3) + 8H^2O$, was once obtained by saturating an insoluble acid lithium molybdate with lithium carbonate (Delafontaine). The *thallium salt*, $Tl^2O.MoO^3$, is obtained as a crystalline powder, by boiling aqueous thallious oxide with molybdic anhydride, or as a white curdy precipitate by mixing the hot aqueous solutions of thallious sulphate and sodium molybdate. It is slightly soluble in water, melts at a red heat, and gives off black-brown vapours when fused with sodium carbonate (Delafontaine). The *magnesium salt*, $MgO.MoO^3 = 7H^2O$, remains, on evaporating the solution formed by boiling magnesia with water and molybdic anhydride, in groups of thin, vitreous, efflorescent prisms, which give off their water without fusion at a red heat (Ullik). By cooling a solution evaporated by heat, Delafontaine obtained monoclinic prisms containing $MgO.MoO^3 + 5H^2O$. The *potassio-magnesic salt*, $K^2O.MgO.2MoO^3 + 2H^2O$, crystallises from a solution of equivalent quantities of the component salts in groups of small vitreous prisms, which give off their water at a moderate heat, and melt without decomposition at a dull red heat; easily soluble in water. The *ammonio-magnesic salt*, $\left.\begin{matrix}(NH^4)^2O\\MgO\end{matrix}\right\}MoO^3 + 2H^2O$, obtained in like manner, forms larger crystals isomorphous with the preceding.

Dimolybdates. $RO\,.\,2MoO^3$.—The *sodium salt*, containing 1 mol. water according to Struve, anhydrous according to Ullik, is produced by adding 1 mol. molybdic anhydride to 1 mol. fused sodium nitrate, and remains in silky needles when the undecomposed half of the nitrate is dissolved out by water. Potassium nitrate is likewise only half decomposed by molybdic anhydride, but the resulting potassium bimolybdate is very easily decomposible and cannot be obtained pure (Ullik).

Seven-thirds Molybdates. $3RO\,.\,7MoO^3 + nH^2O$.—The *potassium salt*, $3K^2O\,.\,7MoO^3 + 4H^2O$ (described by Svanberg a. Struve as a compound of the bi- and tri-molybdate), is always formed when molybdic acid is evaporated to dryness with potassium carbonate even in excess, the pulverulent residue dissolved in the smallest possible quantity of water, and the solution left to evaporate. It forms small, deeply striated monoclinic prisms, which melt without decomposition at a red heat, and give off their water at a lower temperature. They are decomposed by water, depositing trimolybdate:

$$3K^2O\,.\,7MoO^3 = 2(K^2O\,.\,3MoO^3) + K^2O\,.\,MoO^3$$

(Delafontaine). The *sodium salt*, $3Na^2O\,.\,7MoO^3 + 22H^2O$, crystallises on cooling from a hot solution of molybdic acid in sodium carbonate mixed with nitric acid, in transparent well-defined prisms; by slow evaporation, in larger opaque rectangular tables, which effloresce rather quickly in dry air, give off 21 mol. water at 100°, the last molecule at 200°, and may also be fused without decomposition (Delafontaine). According to Ullik it separates from a solution of 1 mol. sodium trimolybdate mixed with 1 mol. sodium carbonate, in large transparent crystals which lose 8 mol. water by efflorescence, 21 mol. at 100°, and the last between 120° and 130°. When treated with different quantities of sodium carbonate, a corresponding portion of it is converted into the monomolybdate, the rest remaining undecomposed. The *ammonium salt*, $3(NH^4)^2O\,.\,7MoO^3 + 4H^2O$, is the salt formerly described (iii. 1037) as a bimolybdate (Delafontaine; Ullik). A *sodio-ammonic salt*, $2\frac{1}{3}(NH^4)^2O\,.\,\frac{2}{3}Na^2O\,.\,7MoO^3 + 5H^2O$, obtained by adding nitric acid to a mixed solution of sodium and ammonium molybdates, crystallises in small striated rhombic or monoclinic prisms (Delafontaine).

The *magnesium salt*, $3MgO\,.\,7MoO^3 + 20H^2O$, crystallises by spontaneous evaporation from a solution of 7 mol. magnesium monomolybdate mixed with 4 mol. nitric acid, in radiate groups of transparent, vitreous, tabular, oblique prisms. It is permanent in the air, gives off all its water without decomposition at a red heat, and is moderately soluble even in cold water (Ullik).

Trimolybdates, $RO\,.\,3MoO^3 + H^2O$, are obtained by boiling the carbonates of the several bases with water and excess of molybdic anhydride (4 mol. MoO^3 to 1 mol. base), whereby quadromolybdates are formed in the first instance, and decompose when the solutions are slowly evaporated; also by mixing the solution of a less acid molybdate with any acid in not too large a quantity (the precipitates formed in solutions of molybdates by acids always consist, according to Ullik, of acid salts, never of pure molybdic anhydride). The solutions of the trimolybdates are coloured light red by potassium ferrocyanide. They crystallise by slow evaporation in cauliflower-like aggregates of nodular crystalline groups, and dissolve freely in hot, very slightly in cold water. By more rapid evaporation, especially of small quantities, amorphous salts are obtained with different quantities of water. The following trimolybdates have been obtained by Ullik:

$K^2O\,.\,3MoO^3 + 3H^2O$, becomes anhydrous at 100°.
$Na^2O\,.\,3MoO^3 + 7H^2O$, crystallised; gives off $6H^2O$ at 100°.
$Na^2O\,.\,3MoO^3 + 4H^2O$, amorphous.
$CaO\,.\,3MoO^3 + 6H^2O$.
$MgO\,.\,3MoO^3 + 10H^2O$.
$CoO\,.\,3MoO^3 + 10H^2O$.
$ZnO\,.\,3MoO^3 + 10H^2O$.
$CuO\,.\,3MoO^3 + 9H^2O$, crystallised.
$CuO\,.\,3MoO^3 + 6\frac{1}{2}H^2O$, amorphous.

The *rubidium salt*, $Rb^2O\,.\,3MoO^3 + 2H^2O$, obtained by fusing rubidium carbonate with excess of molybdic anhydride, and dissolving the fused mass in boiling water, crystallises on cooling in small shining six-sided prisms, easily soluble in hot, sparingly in cold water (Delafontaine).

Tetramolybdates, $RO.4MoO^3 + nH^2O$, are contained, according to Ullik, in the solutions which yield the trimolybdates by spontaneous evaporation. When these solutions (which are coloured dark red by potassium ferrocyanide), in the concentrated state, are quickly evaporated on a glass plate, they leave amorphous, transparent, easily soluble masses, which have the composition of quadromolybdates, are permanent in close vessels, but become opaque and are converted into trimolybdates in contact with the air. In the crystalline form they appear to separate only from solutions likewise containing other salts, sodium chloride for example. Ullik has obtained an *amorphous sodium salt*, $Na^2O.4MoO^3 + 5\frac{1}{2}H^2O$, usually of slight greenish or bluish colour; a *crystallised sodium salt*, $Na^2O.4MoO^3 + 6H^2O$, by adding 3 mol. hydrochloric acid to a solution of 4 mol. of the neutral salt; a *calcium salt*, $CaO.4MoO^3 + 9H^2O$, in brownish amorphous masses, fusing with decomposition at a red heat; and a bluish-green *zinc salt*, $ZnO.4MoO^3 + 8H^2O$, behaving like the calcium salt when heated.

Octomolybdates, $RO.8MoO^3 + nH^2O$, are formed by treating any of the preceding salts with a sufficient quantity of one of the stronger acids (7 mol. acid to 1 mol. of a neutral molybdate). They all crystallise, and apparently in perfectly similar forms (oblique rhombic prisms with basal end-face), are extremely soluble in water, and their solutions form a red-brown precipitate with potassium ferrocyanide. The *sodium salt*, $Na^2O.8MoO^3 + 17H^2O$, gives off $14H^2O$ at 100°, the rest between 160° and 180°, melts below a red heat, and decomposes at a higher temperature. The *potassium salt*, $K^2O.8MoO^3 + 13H^2O$, separates from a hot solution on cooling, in small shining crystals, converted by drenching with water into a white sparingly soluble powder. The *magnesium salt*, $MgO.8MoO^3 + 20H^2O$, forms efflorescent prisms, melting with partial decomposition at a red heat. The *barium salt*, $BaO.MoO^3 + 18H^2O$, separates from the acid solution in vitreous prisms insoluble in cold water, and decomposed by hot water. The *calcium salt*, $CaO.8MoO^3 + 18H^2O$, crystallises in very small prisms, easily soluble in hot, nearly insoluble in cold water. Both these salts decompose like the magnesium salt when heated (Ullik).

Decamolybdates.—The *sodium salt*, $Na^2O.10MoO^3 + 21H^2O$, is produced by dissolving the heptahydrated trimolybdate or sodium carbonate in the corresponding quantity of soluble molybdic acid, and leaving the solution to evaporate; it resembles the octomolybdate with $17H^2O$, and is very soluble in water. $Na^2O.10MoO^3 + 12H^2O$ separates as a white crystalline, sparingly soluble powder, when a solution of the salt $Na^2O.MoO^3 + 2H^2O$ is heated on the water-bath with a quantity of hydrochloric acid equivalent to the sodium present.

Hexdecamolybdates.—The *sodium salt*, $Na^2O.16MoO^3 + 9H^2O$, separates as a fine white insoluble powder when a solution of the normal sodium salt in a small quantity of water is heated to boiling with a large excess of strong nitric acid. When a solution of 1 mol. sodium carbonate is poured upon 1 mol. of this salt, carbon dioxide is given off, and there remains a white pulverulent sparingly soluble octomolybdate, $Na^2O.8MoO^3 + 4H^2O$. The latter salt is also formed when 2 mol. sodium carbonate are used; but in this case a soluble molybdate is likewise produced, and on evaporating the solution, the salt $Na^2O.3MoO^3 + 7H^2O$ crystallises out.

Ullik has also obtained double molybdates in which part of the molybdenum is replaced by sulphur or chromium. A mixed solution of ammonium sulphate and magnesium molybdate, or of magnesium sulphate and ammonium molybdate, yields well-defined crystals having the composition of the double sulphate $Mg(NH^4)^2(SO^4)^2 + 6H^2O$, in which variable quantities of sulphur are replaced by molybdenum, without essential alteration of the crystalline form. When hot strong solutions are used and the mixture is left to crystallise by cooling, or when a considerable excess of ammonium molybdate is added, the crystals are rich in molybdic acid; but by spontaneous evaporation of dilute solutions, crystals are formed containing a smaller proportion of molybdic acid. The latter are permanent, whereas the former give off water and ammonia on exposure to the air. In six such salts, the proportion of SO^3 was found to vary from 16·46 to 41·79 p. c., and that of MoO^3 from 38·56 to 3·43 p. c. All the crystals were isomorphous with the known double salts of the magnesium group. A solution of equivalent quantities of neutral magnesium molybdate and neutral potassium chromate yielded by slow evaporation small light yellow crystals of the salt $\left.\begin{matrix}K^2O\\MgO\end{matrix}\right\} . \left\{\begin{matrix}MoO^3\\CrO^3\end{matrix}\right. + 2H^2O$, easily soluble in water, and resembling potassio-magnesic molybdate in their form and their behaviour at high temperatures.

Fluomolybdates. These salts are formed by dissolving the neutral and acid molybdates in hydrofluoric acid. They are mostly easily soluble, crystallise well, and are isomorphous with the corresponding compounds of tin, titanium, and zirconium. The *neutral potassium salt*, $K^2MoF^4O^2 + H^2O$, crystallises from a solution of potassium molybdate slightly supersaturated with hydrofluoric acid, in very thin octagonal tables, which, according to Marignac's determinations, belong to the triclinic system and agree nearly in their angles with the crystals of fluotungstate of potassium, although the latter, according to Marignac, is monoclinic. It is not altered by exposure to the air, gives off its water below 100°, melts at a red heat, and is converted by prolonged fusion in moist air into neutral potassium molybdate, with evolution of hydrofluoric acid. The *acid potassium salt*, $K^2Mo^2F^6O^4 + 2H^2O$, obtained by dissolving the neutral salt in hydrofluoric acid, or by treating acid potassium molybdate with hydrofluoric acid and evaporating, crystallises on cooling in transparent silky needles, which after gentle heating in contact with the air, leave a residue of potassium bimolybdate, but when quickly heated give off molybdic fluoride. The *neutral sodium salt*, $2Na^2MoF^4O^2 + H^2O$, separates from the acid solution in crystalline grains, behaving like the potassium salt when heated, but more soluble. The *acid rubidium salt*, $Rb^2Mo^2F^6O^4 + 2H^2O$, crystallises on cooling from the warm solution of rubidium trimolybdate in hydrofluoric acid, in scaly groups of slender needles, having when dry the aspect of potassium tantalofluoride. It is easily soluble in water, and behaves like the preceding when heated. The *neutral ammonium salt*, $(NH^4)^2MoF^4O^2 + H^2O$, obtained by supersaturating the solution of ordinary ammonia molybdate with ammonia, slightly acidulating with hydrofluoric acid, and evaporating, crystallises in six- or eight-sided tables, isomorphous with the neutral potassium salt. When heated in an open dish, it melts to a pasty mass, gives off vapours of water, hydrofluoric acid, and molybdic fluoride, and when heated to low redness, leaves a residue of molybdic anhydride. The *acid salt*, $(NH^4)^2Mo^2F^6O^4 + 2H^2O$, crystallises in rhombic prisms isomorphous with acid ammonium fluotungstate. The *neutral thallium salt*, $Tl^2MoF^4O^2 + H^2O$, is formed on mixing the neutral potassium salt with thallious sulphate, as a curdy precipitate, which dissolves when warmed and separates again as a crystalline powder on cooling. From a warm solution of neutral thallious molybdate in hydrofluoric acid, it crystallises on cooling in shining straw-yellow rhombic prisms, $\infty P . \infty \bar{P} \infty . \bar{P} \infty$. The crystals melt below a red heat, and when roasted leave the neutral molybdate. The *neutral fluomolybdates of zinc, cadmium, cobalt*, and *nickel* are obtained by dissolving equivalent quantities of the corresponding oxides or carbonates in hydrofluoric acid, and evaporating the solutions, in well-defined crystals of the hexagonal system (six-sided prisms with an acuter or obtuser rhombohedron). The composition of all these salts is represented by the formula $R''MoF^4O^2 + 6H^2O$. They are isomorphous with the corresponding titanofluorides, zircofluorides, and fluoniobates. The zinc and cadmium salts are colourless; the cobalt salt is dark red; the nickel salt light green. They are permanent in dry air (the cadmium salt inclined to effloresce), leave nearly pure molybdic oxide when quickly heated, and neutral molybdates when carefully roasted (Ullik, *loc. cit.*).

Phosphomolybdic Acids. Debray (*Bull. Soc. Chim.* [2] x. 369) has obtained two of these compounds, viz. $P^2O^5.20MoO^3$ and $P^2O^5.5MoO^3$. The former is produced when the precipitate formed by ammonium molybdate in the acidulated solution of a phosphate is boiled with nitromuriatic acid, and the liquid is left to evaporate. It crystallises from this solution in yellow oblique rhombic prisms containing 13·3 p. c. water, which nearly agrees with the formula $P^2O^5.20MoO^3 + 26H^2O$. The aqueous solution of these crystals yields by spontaneous evaporation a second hydrate, $P^2O^5.20MoO^3 + 52H^2O$, containing 23·4 p. c. water, and crystallising in large regular octohedrons; a third, $P^2O^5.20MoO^3 + 40H^2O$, containing 19·4 p. c. water, separates from highly concentrated solutions mixed with a large quantity of nitric acid in less developed and more easily alterable rhombic prisms. Phosphomolybdic acid separates potash, rubidia, cæsia, thallia, ammonia, and the organic bases, but not soda and lithia, from their strongly acidulated solutions, in the form of yellow precipitates. The potassium, ammonium, and thallium salts have the composition $3R^2O.P^2O^5.20MoO^3$ or $R^3PO^4.10MoO^3$, the two former containing 3 mol. (or 3½ mol.) water. The potassium and thallium salts melt at a dull red heat to oily liquids which solidify in the crystalline form on cooling. The ammonium salt is obtained in small yellow highly lustrous crystals when solutions of sodium pyrophosphate and acid ammonium molybdate are mixed together, the precipitates then forming slowly as the pyrophosphate in the liquid becomes converted into orthophosphate. Neutral solutions of silver nitrate give with phosphomolybdic acid a precipitate which gradually changes into microscopic crystals consisting of $2Ag^2O.P^2O^5.20MoO^3 + 7H^2O$. In acid solutions the salts of the heavy metals give no precipitates; hence phosphomolybdic acid crystallises unaltered from a strongly acidulated solution of bismuth. This acid, however, as well as its salts, is stable only in acid solutions. With alkalis it forms molybdates and salts of the second phosphomolybdic acid, $P^2O^5.5MoO^3$, according to the equation:

$$P^2O^5.20MoO^3 + H^2O = P^2O^5.5MoO^3.H^2O + 15MoO^3.$$

The salts of this second phosphomolybdic acid are colourless or slightly coloured, crystallise well, have a mother-of-pearl aspect, and are easily soluble. By excess of acid they are reconverted, with separation of phosphoric acid, into yellow phosphomolybdates:

$$4(P^2O^5.5MoO^3) + 10H^2O = 3(P^2O^5.3H^2O) + P^2O^5.20MoO^3 + H^2O.$$

Treated with a small quantity of acid, they yield salts having the composition $5R^2O.2P^2O^5.10MoO^3 + H^2O$. The anhydride $P^2O^5.5MoO^3$ cannot be isolated, on account of its instability. Of its salts the following have been prepared:

Ammonium salt,	$3(NH^4)^2O.P^2O^5.5MnO^3 + 7H^2O.$
Potassium salt,	$3K^2O.P^2O^5.5MnO^3 + 7H^2O.$
Sodium salt,	$3Na^2O.P^2O^5.5MnO^3 + 14H^2O.$
Silver salt,	$3Ag^2O.P^2O^5.5MnO^3 + 7H^2O.$

The existence of the above-described compounds, and the frequently occurring of molybdates, together with vanadates, lead to the supposition that the constitution of molybdic anhydride is analogous to that of vanadic anhydride, and represented by the formula Mo^2O^5 ($Mo^v = 80$). The phosphomolybdic anhydrides would then have the simpler formulæ $P^2O^5.12Mo^2O^5$ and $P^2O^5.3Mo^2O^5$. But the vapour-density of molybdic chloride does not agree with this hypothesis.

MORESNETITE. A zinc-aluminic silicate from the Altenberg, near Aachen; mostly dark green to leek-green and opaque, sometimes light emerald-green and translucent. Fracture, small conchoïdal. Hardness = 2·5. Streak, white.

	SiO^2	Al^2O^3	ZnO	FeO	NiO	CaO	MgO	H^2O		
Light green .	30·31	13·68	43·41	0·27	1·14	traces		11·37	=	100·18
Dark green .	29·36	13·02	37·98	5·61	0·24	0·76	0·54	11·34	=	98·85

Hence the formula $9(2ZnO.SiO^2) + 2(2Al^2O^3.3SiO^2) + 20H^2O$ (H. Risse, *Jahresb.* 1866, p. 940).

MORIN (Hlasiwetz a. Pfaundler, *J. pr. Chem.* xciv. 65).—The colouring matter of old fustic (iii. 1047). When completely dehydrated by prolonged drying at 100° in a stream of dry air, or by heating to 200°–250°, it has the composition $C^{12}H^8O^5$; *morin hydrate* or *moric acid* is $C^{12}H^{10}O^6$ or $C^{12}H^8O^5.H^2O$. *Potassium morate*, $C^{12}H^9O^6K$, crystallises from a warm solution in concentrated aqueous potassium carbonate, in soft yellow needles, greenish-brown after drying, and recrystallisable only from solution of potassium carbonate. The *sodium-compound* exhibits similar characters. *Calcium morate*, $(C^{12}H^9O^6)^2Ca$, is formed as a yellow precipitate on mixing potassium morate with calcium chloride. *Zinc morate*, $(C^{12}H^9O^6)^2Zn$, is formed by boiling an alcoholic solution of morin with a little sulphuric acid and zinc, in lemon-yellow needles insoluble in water, but soluble in alkalis. In dry ammonia gas, morin assumes a deep yellow colour, and increases in weight by 12·3 p. c. *Bromomoric acid*, $C^{12}H^7Br^3O^6$, formed by triturating moric acid with bromine, crystallises from alcohol in microscopic needles mostly grouped in tufts.

When an alkaline solution of moric acid is treated with sodium-amalgam, the liquid first becomes indigo-blue, then green, finally yellow, and at the end of the reaction contains phloroglucin, formed according to the equation: $C^{12}H^{10}O^6 + H^2 = 2C^6H^6O^3$. When an alcoholic solution of morin acidulated with hydrochloric acid is treated with sodium-amalgam, it turns purple-red, and finally also yields phloroglucin; if, however, before the reaction is complete, the deep purple solution decanted from the sodium-amalgam be evaporated over the water-bath, it deposits purple-red prisms of a body having the same composition as morin, and therefore designated as isomorin. This substance heated either alone or in alcoholic solution, or more quickly by treatment with alkalis, is reconverted into ordinary morin, even when the air is completely excluded. Its solution mixed with alum exhibits a characteristic dichroïsm. Morin fused with potash yields phloroglucin, together with a little oxalic acid.

Morin in alcoholic solution is not fluorescent, but exhibits a beautiful green fluorescence, like that of uranium glass, on addition of an aluminium salt. Zinc salts produce a faint yellow fluorescence, which becomes very deep on addition of alum. Many metallic salts produce no fluorescence in a solution of morin, and prevent the development of that produced by aluminium salts. Acetic, hydrochloric, nitric, sulphuric, phosphoric, and arsenious acids neither produce fluorescence nor prevent that developed by aluminium salts. Boric acid produces a yellow, silicofluoric acid a dark green fluorescence. A morin solution rendered fluorescent by aluminium acetate deposits on boiling a yellow compound of morin and alumina, and the solution then no longer exhibits fluorescence. Morin is oxidised by chromic acid, and the oxidised product no longer gives rise to fluorescence. Silver nitrate oxidises it, with separation of silver, but the filtered liquid, if it has not been heated, exhibits a beautiful yellow fluorescence. Auric chloride acts in the same manner. The alcoholic solution of the aqueous extract of Kuba wood (the best kind of fustic, *Morus tinctoria*) is dark garnet-red by transmitted light, and fluorescent with dark green colour by reflected light. Alum or any aluminium salt added to this solution much diluted with alcohol, produces the green fluorescence above mentioned, which must be due to the morin contained in the extract, inasmuch as solutions of maclurin do not produce it (Goppelsröder, *J. pr. Chem.* ci. 406; civ. 10; *Zeitschr. f. Chem.* [2] iv. 154, 607).

MORINDIN or **MORINDONE.** According to W. Stein (*J. pr. Chem.* xcvii. 234; *Jahresb.* 1866, p. 645), morindin is not identical with ruberythric acid, as supposed by Rochleder (iii. 1048), being distinguished from the latter by its insolubility in ether, the violet colour of its barium-compound, and its reaction with potash. It melts at 245°, but yields even below that temperature a crystalline sublimate of morindone. This latter substance is regarded by Stein as different from alizarin, on account of its giving somewhat different coloured reactions with sulphuric acid and with ferric chloride. He assigns to morindone the formula $C^{14}H^8O^5$. From the experiments of Stenhouse, however, morindone appears to be identical with alizarin (iii. 1048).

MOROXOLITE. A potassio-ferric sulphate, $K^2O(Na^2O)SO^3 + 4(Fe^2O^3.SO^3)$, from an American locality (Shepard, *Jahresb.* 1866, p. 952).

MORPHINE. $C^{17}H^{19}NO^3$.—This alkaloïd, in contact with a solution of *molybdic acid* in strong sulphuric acid, assumes a violet colour, changing to blue and dingy green. With solid *nitrates*, especially those of potassium, sodium, and mercury, the sulphuric acid solution of morphine forms after a while a blood-red zone, and with the dissolved salts a violet liquid, changing to brown or brownish-yellow (Fröhde, *Zeitschr. anal. Chem.* v. 214).

On the characters of sublimed morphine, see ALKALOÏDS (p. 87).

An aqueous solution of a morphine salt mixed with excess of *iodine*, deposits a crystalline precipitate of a tetriodide, $C^{17}H^{19}NO^3HI^4$, which may be recrystallised from a strong solution of potassium iodide, but not from alcohol (Jörgensen, *Zeitschr. f. Chem.* [2] v. 673).

A compound of morphine and *zinc chloride*, $C^{17}H^{19}NO^3.ZnCl^2 + 2H^2O$, is obtained in vitreous granules by mixing the alcoholic solutions of the two bodies, carefully dissolving out the separated zinc oxide by hydrochloric acid, and cooling the hot filtrate. The salt is also said to crystallise with 7 mol. water (Gräfinghoff, *Jahresb.* 1865, p. 446).

Estimation of Morphine in Opium.—1. Two grams of chopped opium are macerated with 8 c. c. of a solution of ammonium oxalate (to decompose the calcium meconate), triturated after some hours, then thrown on a filter, and washed with 5 c. c. water. The filtrate mixed with an equal volume of 80 p. c. alcohol, and then with ammonia to alkaline reaction, is left for 24 hours in a closed flask and frequently agitated, and the flask is washed out with a small quantity of 40 p. c. alcohol. The dried filter with its contents is returned to the uncleansed flask, and after addition of a few drops of the alcoholic tincture of St. Martha wood, is treated with a slight excess of an exactly measured titrated solution of oxalic acid, containing 4·42 crystallised acid in a litre, of which from 10 to 15 c. c. are sufficient (the acid liquid turns yellow), then diluted with 100 c. c. water, and the excess of acid is determined by means of a dilute titrated solution of soda. Each cub. cent. of the oxalic acid solution corresponds to 0·2 p. c. morphine (Fleury, *J. Pharm.* [4] vi. 99).

2. Guilliermond (*ibid.* vi. 102) gives the following modifications of his former process (iii. 1053). Fifteen grams of opium are triturated to complete comminution

with 120 c. c. of 70 p. c. alcohol; the mixture is introduced into a glass vessel and repeatedly agitated, after the weight has been made up, if necessary, to 125 grams; the liquid is filtered after a while; and 80 c. c. of the filtrate (containing 10 grm. opium) are introduced into a wide stoppered glass. Two grams of the ammoniacal liquid are then transferred by means of a drawn-out pipette to the bottom of the vessel, and the stopper is introduced without allowing the two liquids to mix. After 36 hours the morphine is found separated in thick reddish crystals, the narcotine in slender white needles; the two alkaloïds are separated by levigation, and the morphine is washed with boiling water. Stronger or weaker spirit is not so well adapted for the separation. As, however, a considerable quantity of morphine remains dissolved in the 70 p. c. alcohol ($\frac{1}{8}$ of the whole amount, according to Guilliermond), the results obtained by this process are not absolute, but only comparable under similar conditions.

3. Schachtrupp (*Zeitschr. anal. Chem.* vii. 284, 509) describes a method founded on the solubility of narcotine and the insolubility of morphine in benzol, and the easy solubility of morphine in amylic alcohol. A weighed quantity of opium is treated with a solution of sodium carbonate till the opium is completely comminuted; the still alkaline mixture is evaporated over the water-bath; the dry dusty residue is digested several times with hot benzene; the filter through which the liquid has passed is added to the residue; the remainder of the benzene is evaporated off; and the residue is exhausted with boiling amylic alcohol. The greater part of the morphine then crystallises from the united extracts on cooling. The amylic alcohol is decanted and the greater part of it distilled off; the brown residue is agitated while still hot with water containing hydrochloric acid; the crystals previously obtained are dissolved in the same liquid; and the solution is evaporated to twice the weight of the opium used, then filtered, and precipitated with ammonia. The morphine thus separated, which is still coloured, but otherwise pure, is collected after 24 hours, washed, dried, and weighed. Two samples of Smyrna opium thus treated yielded 8·30 and 8·29 p. c. morphine; the same samples treated by Merck's process gave respectively 7·96 and 8·01 p. c.

For the preparation of morphine also, Schachtrupp recommends the treatment of opium with sodium carbonate, and preliminary exhaustion of the dried mass with hot benzene. The residue again dried is drenched with water; strong acetic acid is added; the mixture warmed for some time and strained; and the undissolved portion is treated several times in the same manner. The united extracts evaporated down to twice the weight of the opium used are mixed with a slight excess of ammonia, and the morphine which separates after some time is redissolved in acetic acid and precipitated by ammonia. For final purification it is dissolved in boiling amylic alcohol, from which it separates in colourless crystals without the use of animal charcoal.

Derivatives of Morphine.

Apomorphine or **Apomorphia.** $C^{17}H^{17}NO^2$ (Matthiessen a. Wright, *Proc. Roy. Soc.* xvii. 455, 460).—An organic base differing from morphine by containing H^2O less, and produced: 1. By heating morphine in a sealed tube to 140°–150° for two or three hours with a large excess of hydrochloric acid:

$$C^{17}H^{19}NO^3 = H^2O + C^{17}H^{17}NO^2.$$

2. From codeine (which has the composition of methyl-morphine) by similar treatment:

$$\underset{\text{Codeine.}}{C^{18}H^{21}NO^3} + HCl = \underset{\substack{\text{Methyl-}\\\text{chloride.}}}{CH^3Cl} + H^2O + \underset{\text{Apomorphine.}}{C^{17}H^{17}NO^2}$$

The methyl chloride formed in the second case collects on cooling on the top of the tarry contents of the tube, and escapes as gas when the tube is opened. The residue in this or in the first process contains the hydrochloride of apomorphine, and when dissolved in water, and precipitated by sodium carbonate, yields, on extraction with ether and agitation with hydrochloric acid, crystalline hydrochloride of apomorphine, from which the base may be precipitated by sodium bicarbonate, as a snow-white crystalline mass, which quickly turns green on exposure to the air. The green mass is partly soluble in water, communicating to it a fine emerald colour, in alcohol with green, in ether and benzene with splendid rose-purple, and in chloroform with violet colour.

Hydrochloride of apomorphine may also be prepared by digesting morphine with excess of hydrochloric acid under paraffin on the water-bath for some days. It is anhydrous. When exposed to the air in the moist state, or heated in the dry state, it turns green, like the free base, probably from oxidation, as it exhibits an increase of weight.

Apomorphine differs greatly from morphine in its relations to solvents and reagents. It is soluble in alcohol, ether, and chloroform, whereas morphine is almost insoluble in the last two liquids, and but sparingly soluble in cold alcohol. In water apomorphine is slightly soluble, especially in presence of carbonic acid, whereas morphine is nearly insoluble.

The following comparative reactions are exhibited by solutions containing each 1 per cent. of the hydrochloride of the base:

Reagents	Morphine	Apomorphine
Caustic potash	No pp. Stronger solutions give a white pp. easily soluble in excess, without decomposition	White pp. soluble in excess, speedily blackening
Ammonia	No pp. Stronger solutions give a crystalline white pp. insoluble in excess	White pp. soluble in excess, very speedily blackening
Lime-water	No pp. Morphia dissolves readily in lime-water	White pp. soluble in excess, slowly darkening
Sodium bicarbonate	No pp. Stronger solutions yield a white unalterable pp. slightly soluble in excess	White pp. slightly soluble in excess, turning green
Strong nitric acid	Yellow-orange colour, almost bleached on warming	Blood-red colour, becoming paler on warming
Neutral ferric chloride	Greenish-blue colour. Morphine alone gives a pure blue colour	Dark amethyst colour
Potassium dichromate	—	Dense yellow-orange pp., soon decomposing
Potassium dichromate and strong sulphuric acid	—	Dark red coloration
Silver nitrate	Very slowly reduced	Quickly reduced, even in the cold
Potassium iodide	— No pp. with concentrated solution	White non-crystalline pp. speedily becoming green
Platinic chloride	— Yellow crystalline pp. in stronger solutions	Yellow pp.; decomposes on warming
Mercuric chloride, sodium phosphate, ammonium oxalate	The morphine precipitates with these reagents are much more soluble than the corresponding precipitates of apomorphine	

The physiological action of apomorphine is also very different from that of morphine; a very small dose of the former speedily produces vomiting and considerable depression, but this soon passes off, leaving no ill effects. The hydrochloride is a non-irritant emetic and powerful antistimulant; $\frac{1}{10}$ of a grain of this salt subcutaneously injected, or $\frac{1}{4}$ gr. taken by the mouth, produces vomiting in from four to ten minutes.

Oxymorphine. $C^{17}H^{19}NO^4$ (Schützenberger, *Bull. Soc. Chim.* [2] iv. 176).—When a solution of morphine hydrochloride is heated to 60° with an equivalent weight of silver nitrite, nitrogen dioxide is evolved free from carbon dioxide, the liquid becoming yellow and slightly alkaline. At the end of the reaction the precipitated silver chloride contains the greater part of the morphine in the form of oxymorphine, which may be separated from the silver chloride by solution in water containing hydrochloric acid. The *hydrochloride*, $C^{17}H^{19}NO^4.HCl$, thus obtained, crystallises in microscopic needles easily soluble in hot water, insoluble in alcohol; it has a slightly bitter taste, and does not appear to be poisonous. Ammonia separates the *base* in the form of a powder which redissolves in a large excess of the precipitant, and separates in small needles on boiling. It is quite insoluble at the boiling heat in water, alcohol, and ether, has no taste, melts at about 245°. The *platinochloride*, $2(C^{17}H^{19}NO^4.HCl).PtCl^4$, is an amorphous yellow powder easily decomposed by heating with platinic chloride. The *sulphate*, $4C^{17}H^{19}NO^4.H^2SO^4$ (at 140°), is slightly soluble in cold water, and separates in small needles on mixing the hydrochloride with sulphuric acid.

By the prolonged action of silver nitrite on morphine hydrochloride, another base is produced closely allied to the preceding, namely oxymorphine hydrate, $C^{17}H^{21}NO^5$. It dissolves more readily in cold ammonia, and separates therefrom at the boiling heat in crystalline grains (compare iv. 313).

MUCEDIN. This name is applied by Ritthausen to a constituent of wheat-gluten soluble in alcohol, and to a similar, if not identical compound, forming part of the protein-substance of rye. Wheat-mucedin was formerly called *mucin*. Respecting the preparation and properties of these substances, see Ritthausen (*J. pr. Chem.* xci. 296; xcix. 439; *Bull. Soc. Chim.* [2] viii. 132; *Jahresb.* 1864, p. 625; 1866, p. 716; *Gmelin's Handbook*, xviii. 443, 444). The gelatinous substance of the vineyard snail (*Helix pomatia*) is also called mucin by E. Eichwald, who has described its preparation and properties (*Ann. Ch. Pharm.* cxxxiv. 177; *Bull. Soc. Chim.* [2] v, 308; *Jahresb.* 1868, p. 649; *Gmelin's Handbook*, xviii. 340–347).

MUCOBROMIC, MUCOCHLORIC, and **MUCONIC ACIDS.** See PYROMUCIC ACID, iv. 763; also v. 1093.

MURRAYIN. $C^{36}H^{44}O^{20}$ (Blas, *Zeitschr. f. Chem.* [2] v. 316).—A glucoside, prepared by de Vrij from *Murraya exotica*, an East Indian plant. It occurs in all parts of the plant, but chiefly in the petals. These are repeatedly exhausted with boiling water; the evaporated extract is treated with cold water to remove colouring matter, extractive matter, &c.; and from the undissolved residue, murrayin, and a product of its decomposition, murrayetin, are extracted by absolute alcohol. The latter is precipitated by an alcoholic solution of lead acetate; the remaining liquid, freed from lead by hydrogen sulphide, is evaporated to dryness; the residue is dissolved in the smallest possible quantity of absolute alcohol; and the solution, decolorised with animal charcoal, is left to crystallise.

Murrayin is a white light powder consisting of small needles, inodorous, slightly bitter, and not at all poisonous. It dissolves sparingly in cold, easily in boiling water and alcohol, but is insoluble in ether; the solutions have a neutral reaction, and leave the murrayin, when evaporated, in the form of an amorphous jelly. Murrayin crystallises from absolute alcohol. The air-dried crystals contain $C^{36}H^{44}O^{20} + H^2O$; they give off 1 mol. water (2·7 p. c.) at 115°, and the residue melts at 170°. Murrayin dissolves easily in alkalis and alkaline carbonates; the concentrated solutions quickly turn yellow, become brown when heated, and are decolorised by acids without precipitation. The alkaline solutions exhibit a yellow fluorescence by transmitted, greenish-blue by reflected light. The aqueous solution does not exhibit this fluorescence; but the addition of the smallest quantity of murrayetin developes it immediately. The aqueous solution is not precipitated by iron, copper, mercury, or lead-salts, excepting basic lead acetate. Murrayin reduces ammoniacal silver solution at a gentle heat, and Fehling's solution at 100°. Strong sulphuric acid dissolves it with deep yellow colour. By heating with dilute sulphuric or hydrochloric acid, it is resolved into murrayetin and glucose:

$$C^{36}H^{44}O^{20} + 2H^2O = C^{24}H^{24}O^{10} + 2C^6H^{12}O^6.$$

Murrayetin crystallises in needles aggregated into a white, light, silky mass;

sometimes also in rhombic prisms. The crystals contain $C^{24}H^{24}O^{15}.H^2O$, and give off their water (3·6 p. c.) over sulphuric acid. Murrayetin heated in an air-bath between watch-glasses melts at 100°, and sublimes partially in shining crystals. It is tasteless and scentless, slightly soluble in cold, more freely in boiling water, easily in alcohol, less easily in ether. The concentrated solutions have a faint acid reaction, and all the solutions are fluorescent. Caustic alkalis and alkaline carbonates dissolve murrayetin with yellowish colour, and intensify the fluorescence. These solutions when heated acquire a deeper yellow colour, but lose their fluorescent property, which is moreover not restored by neutralisation. Ferric chloride produces in the aqueous solution a fine blue-green colour; lead acetate a yellow colour; and soon afterwards a yellow precipitate, which is decomposed by washing with water.

MYCO-INULIN. $C^{12}H^{22}O^{11}.H^2O$.—A substance resembling inulin, occurring in a kind of truffle (*Elaphomyces granulatus*). Its aqueous solution is not altered by iodine-water, ferric chloride, ferrous sulphate, mercuric chloride, mercurous nitrate, basic lead acetate, baryta-water, lime-water, or ammonium oxalate. It is neutral, and prevents the precipitation of cupric oxide by caustic soda, but does not reduce it on boiling. Boiled with dilute sulphuric acid, it yields sugar (Ludwig, *Zeitschr. f. Chem.* [2] vi. 668).

MYELIN. Neubauer has shown that the peculiar forms designated by this name (iii. 1069) may be produced in various ways, without the presence of cholesterin or protagon, *e.g.* by adding a drop of ammonia to a drop of oleic acid on the object-glass of a microscope, or a drop of water to the white greasy mixture of oleic acid and ammonia: he therefore regards the production of these forms as a purely physical phenomenon (*Zeitschr. anal. Chem.* vi. 189; *Jahresb.* 1867, p. 781).

MYELOÏDIN and **MYELOÏDIC ACID.** These names are given by Köhler (*Chem. Centr.* 1867, pp. 406, 1022; *Jahresb.* 1867, p. 809) to two phosphoretted bodies which he has extracted from brain. The first is described as neutral and yielding with lead-acetate a precipitate containing $C^{46}H^{79}PbNPO^{10}$; the second is said to yield a lead salt containing $C^{74}H^{133}PbNPO^{28}$.

MYOCTONIC ACID. An oily narcotic acid substance obtained by distilling the acidulated juice of *Palicourea Marcgravii* (Peckolt, *Arch. Pharm.* [2] cxxvii. 93).

MYOSIN. See MUSCULAR TISSUE (iii. 1065).

MYRRH. According to Brückner (*N. Rep. Pharm.* xvi. 76), this gum-resin contains in 100 pts.:

Substances soluble in water (vegetable mucilage and arabin)	67·76
Resin insoluble in ether	4·81
Resin soluble in ether	12·57
Resin soluble in carbon bisulphide	14·06
Substances soluble in alcohol and water	0·43
Insoluble (sand, bark, &c.)	0·38

According to Hlasiwetz a. Barth, myrrh is oxidised slowly and partially by potash, yielding protocatechuic acid and a small quantity of pyrocatechin (*Jahresb.* 1866, p. 630).

N

NAPHTHALENE. $C^{10}H^8$.—On the constitution of this hydrocarbon, see Aromatic Series (p. 212). It is produced, together with others, by the decomposition of several of the aromatic hydrocarbons, when their vapours are passed through a red-hot tube:

$$\underset{\text{Toluene.}}{4C^7H^8} = \underset{\text{Naphthalene.}}{C^{10}H^8} + \underset{\text{Benzene.}}{3C^6H^6} + 3H^2.$$

$$\underset{\text{Xylene.}}{3C^8H^{10}} = \underset{\text{Naphthalene.}}{C^{10}H^8} + \underset{\text{Toluene.}}{2C^7H^8} + 3H^2.$$

$$\underset{\text{Cumene.}}{2C^9H^{12}} = \underset{\text{Naphthalene.}}{C^{10}H^8} + \underset{\text{Xylene.}}{C^8H^{10}} + 3H^2.$$

Also when a mixture of the vapour of benzene, cinnamene, anthracene, or chrysene with ethylene gas is passed through a red-hot tube:

$$\begin{array}{lllllllll} C^6H^6 & + & 2C^2H^4 & = & C^{10}H^8 & + & 3H^2 \\ C^8H^8 & + & C^2H^4 & = & C^{10}H^8 & + & 2H^2 \\ C^{14}H^{10} & + & C^2H^4 & = & C^{10}H^8 & + & C^6H^6 \\ C^{18}H^{12} & + & 2C^2H^4 & = & C^{10}H^8 & + & 2C^6H^6 \end{array}$$

(Berthelot, *Bull. Soc. Chim.* [2] vi. 272, 279; *Jahresb.* 1866, p. 542–545). It occurs in Rangoon petroleum, separating at the temperature of a mixture of ice and salt from the portion which boils between 208° and 209° (corr.) (Warren a. Storer, *Mem. Amer. Acad.* ix. 208).

H. Vohl (*J. pr. Chem.* cii. 29) describes the preparation of naphthalene on the large scale. He finds that when purified by treatment with acids and alkalis and repeated rectification, it has a sp. gr. of 1·15173 at 15°, melts at 79·25°, and boils at 217°–218° (compare iv. 5). When formed into sticks like sulphur, it has the aspect of alabaster, cracks in the warm hand, and becomes negatively electric when rubbed with silk. Fused naphthalene absorbs a large quantity of air, which it gives off again with effervescence shortly before solidifying. Sulphur, phosphorus, and the sulphides of arsenic, antimony, and tin, are easily dissolved by boiling naphthalene, and separate for the most part in the crystalline form on cooling. Indigo is likewise dissolved by it, and remains in the form of slender copper-coloured needles when the cooled mass is treated with alcohol. Iodine, mercuric chloride and iodide, arsenious oxide, succinic, benzoic, and oxalic acids, dissolve with moderate facility in boiling naphthalene. When naphthalene is brought in contact with the strongest nitric acid, HNO^3, a large quantity of water added, and the resulting precipitate, after washing with dilute alcohol, is mixed with a little hydrate and sulphide of potassium, and dried, the residue dissolves in alcohol with violet-red colour.

Decompositions.—1. According to Kletzinsky (*Jahresb.* 1866, p. 561), naphthalene vapour passed through a red-hot tube is resolved into marsh gas and very finely divided carbon, available for making printers' ink, &c. According to Berthelot (*Bull. Soc. Chim.* [2] vi. 281), naphthalene undergoes no alteration at a red heat.—2. It is but slightly altered by heating with hydrogen; at a bright red heat, however, small quantities of benzene and acetylene are produced: $C^{10}H^8 + H^2 = C^6H^6 + 2C^2H^2$.—3. It acts rapidly at a red heat on *acetylene*, apparently forming anthracene: $C^{10}H^8 + 2C^2H^2 = C^{14}H^{10} + H^2$.—4. With *benzene* at a white heat it forms anthracene, $C^{10}H^8 + 3C^6H^6 = 2C^{14}H^{10} + 3H^2$ (Berthelot, *ibid.* vi. 280; vii. 292, 293).

5. Heated to 280° in a sealed tube with 20 pts. of saturated aqueous *hydriodic acid*, it yields a liquid chiefly consisting of naphthalene hydride, $C^{10}H^{10}$ (Berthelot, *Jahresb.* 1867, p. 709). If the heating be continued somewhat longer with 20 pts. of the acid, 3 mol. iodine are separated, and diethyl-benzene, $C^{10}H^{14}$, is produced, together with ethyl-benzene, C^8H^{10}, as the chief product, and a small quantity of benzene. When naphthalene is heated with 80 pts. of saturated hydriodic acid, 19 to 20 mol. iodine are separated to 1 mol. naphthalene, the chief product being decane, $C^{10}H^{22}$, with smaller quantities of octane, hexane, ethane, and free hydrogen. The same products are obtained with perchloronaphthalene, $C^{10}Cl^8$, the octane however predominating.

With 25 pts. acid to 1 pt. naphthalene, the reaction goes on in the same manner as in the last two cases, excepting that carbon is separated, and the more volatile products contain quintane or amyl hydride (Berthelot, *Jahresb.* 1867, p. 709).

6. By boiling with a solution of *potassium permanganate* it is oxidised to phthalic acid, $C^8H^6O^4$, and carbon dioxide. With *sulphuric acid* and *potassium dichromate* (or lead dioxide) it likewise yields phthalic acid, together with dinaphthyl and an acid having the composition $C^{20}H^{14}O^4$. With *sulphuric acid* and *manganese dioxide* the products are phthalic acid, dinaphthyl, and a red resin. The formation of dinaphthyl, $C^{20}H^{14}$, is represented by the equation: $2C^{10}H^8 + O = C^{20}H^{14} + H^2O$ (Lossen, *Ann. Ch. Pharm.* cxliv. 71).

7. Naphthalene heated with *silver oxide* (to 250°) or with *cupric oxide* (to 400°) yields several beautifully crystallising hydrocarbons, among which are C^9H^6, C^8H^6, and C^6H^4.

8. When *potassium chlorate* is added by small portions to a mixture of naphthalene and strong sulphuric acid, chlorous acid is evolved, and acts upon the naphthalene, partly by oxidation, forming phthalic acid and carbon dioxide, partly by direct addition, forming chloroxynaphthalic acid, $C^{10}H^7ClO^5$:

$$C^{10}H^8 + 3ClHO^2 = C^{10}H^7ClO^5 + 2HCl + H^2O,$$

partly so as to form dichloronaphthalene, according to the equation:

$$C^{10}H^8 + Cl^2O^3 = C^{10}H^6Cl^2 + H^2O + O^2.$$

Lastly, a chlorinated sulpho-acid, $C^{10}H^5ClSO^3$, is formed in considerable quantity (Th. Hermann, *Ann. Ch. Pharm.* cli. 1).

9. Naphthalene or bromonaphthalene, heated with *fuchsine*, yields a violet colouring matter, resembling Hofmann's violet, perhaps consisting of rosaniline with 1 at. hydrogen replaced by naphthyl, $C^{10}H^7$ (Balló, *Dingl. pol. J.* cxcv. 82; *Zeitschr. f. Chem.* [2] vi. 283).

Compounds of Naphthalene.

Acenaphthene or *Acetyl-naphthalene*, $C^{12}H^{10} = C^2H^2.C^{10}H^8$, isomeric with diphenyl, has been already described (p. 3).

Respecting the *chlorides of naphthalene*, see CHLORONAPTHALENES (p. 845).

Naphthalene Hydride, $C^{10}H^{10}$, is found amongst the heavy oils of coal-tar boiling between 200° and 220°. It is produced by heating naphthalene to 280° in a sealed tube for a short time with saturated aqueous hydriodic acid (20 pts.). It is a viscid liquid, having a strong disagreeable odour, and boiling between 200° and 210°. Heated to redness in a sealed tube, it is resolved into naphthalene and hydrogen. With cold nitric acid it forms, without evolution of gas, a solution from which water throws down a liquid smelling like naphthalene and nitrobenzene. It is dissolved by strong sulphuric acid with aid of heat; by the fuming acid at ordinary temperatures, forming a sulpho-acid which is soluble in water, and is attacked by bromine with evolution of hydrobromic acid.

Together with the hydride just described there is formed a small quantity of another hydrocarbon boiling at 190°, probably a second naphthalene hydride, $C^{10}H^{12}$ (Berthelot, *Jahresb.* 1867, p. 709).

Napthalene-potassium, $C^{10}H^8K^2$, analogous to the hydride above described, is formed by fusing naphthalene in a glass tube with a small quantity of potassium, removing the black crust which covers the metal by pressure with a glass rod as fast as it forms, and boiling the black pulverulent product with benzol to remove unaltered naphthalene. With water it yields potassium hydrate, and, together with naphthalene, a hydrocarbon ($C^{10}H^{10}$?) more fusible than the latter (Berthelot, *Bull. Soc. Chim.* [2] vii. 110).

Substitution-derivatives of Naphthalene.

Bromonaphthalenes (Glaser, *Ann. Ch. Pharm.* cxxxv. 40).—*Monobromonaphthalene*, $C^{10}H^7Br$, is obtained by mixing a solution of naphthalene in carbon bisulphide with 5 at. bromine, and distilling the liquid which remains after the carbon bisulphide has been driven off. It is a colourless strongly refracting oil, having a sp. gr. of 1·555 and boiling at 285°. Dissolves easily in alcohol and ether; takes up naphthalene and iodine, but does not combine with the latter; is not decomposed by alcoholic potash, but is reconverted into naphthalene by sodium-amalgam. Wahlforss (*Jahresb.* 1865, p. 564), by slowly adding bromine in rather more than the theoretical dissolve a certain quantity of water, which they retain with some degree of obstinacy. Ketones have little or no tendency to take up oxygen from the air, in this respect being different from aldehydes, which have this tendency, and are composed of carbon monoxide with one equivalent of alcohol-radicle and one equivalent of hydrogen; *e.g.*,

$$\text{Common Aldehyde, } CO\left\{\begin{matrix}CH^3\\H\end{matrix}\right. .$$

Ketones undergo very precise oxidation by treatment with a mixture of bichromate of potash and dilute sulphuric acid of a certain strength (viz. a solution containing 8 per cent. of the bichromate, and just enough sulphuric acid to form chrome-alum).

The products of oxidation by means of such a chrome-solution employed at temperatures not exceeding 100° are acids of the acetic series. A very simple law appears to govern the course taken by the oxidation, viz. that the carbon monoxide becomes attached to the lower of the two alcohol-radicles. Thus methyl-amyl ketone gives acetic and valerianic acids:

$$CO\left\{\begin{matrix}CH^3\\C^5H^{11}\end{matrix}\right. + O^3 = C^2H^4O^2 + C^5H^{10}O^2.$$

In accordance with this law, methyl-ethyl ketone gives only acetic acid, and not acetic and propionic acids:

$$CO\left\{\begin{matrix}CH^3\\C^2H^5\end{matrix}\right. + O^3 = 2C^2H^4O^2.$$

In the instance of the simplest possible ketone, viz. dimethyl-ketone, which is common acetone, the products are acetic acid and formic acid, the latter, however, from its instability, rapidly passing into carbonic acid and water on prolonged oxidation:

$$CO\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right. + O^4 = C^2H^4O^2 + CO^2 + H^2O.$$

In the instance of ketones containing any other normal alcohol-radicles, and even when the radicles are to some degree iso-compounds, the oxidation of the ketone by means of the above-mentioned chrome-solution is an operation yielding two atoms of acid with almost mathematical precision. When, however, the alcohol-radicles are in a marked degree iso-radicles, the oxidation becomes irregular. Thus, methyl-isopropyl ketone may be expected to give

$$CO\left\{\begin{matrix}CH^3\\CH(CH^3)^2\end{matrix}\right. + O^6 = 2C^2H^4O^2 + CO^2 + H^2O.$$

Ketones can also take up hydrogen, and thereby pass into secondary alcohols; *e.g.*,

$$CO\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right. + H^2 = C\left\{\begin{matrix}CH^3\\CH^3\\H\\OH\end{matrix}\right.$$

This reaction is effected by the employment of sodium-amalgam in presence of water (Friedel).

Those ketones which contain methyl enter into combination with alkaline bisulphites, and form compounds which are often beautifully crystalline, and from which by distillation with a caustic alkali the ketone may be recovered in its original state. Ketones not containing methyl do not form compounds with alkaline bisulphites, or form them only with the utmost difficulty.

The ketones are produced in the following reactions:

1. By the action of carbon monoxide on the compounds of the alkali-metals: $CO + 2NaC^2H^5 = Na^2 + CO(C^2H^5)^2$ (Wanklyn).

2. By the action of the chloride of an acid-radicle on the zinc-compound of an alcohol radicle: $C^2H^3OCl + Zn(CH^3)^2 = C^2H^3O.CH^3 + ZnClCH^3$ (Pebal a. Freund).

3. By distillation of the baryta- or lime-salts of the fatty acids, this being the original process by which common acetone was first prepared:

$$\left.\begin{matrix}(COCH^3)^2\\Ba''\end{matrix}\right\}O^2 = \left.\begin{matrix}CO\\Ba''\end{matrix}\right\}O^2 + CO(CH^3)^2.$$

If a mixture of the salts of two different fatty acids be employed, the product is a ketone containing different alcohol-radicles (Williamson):

thus obtained was naphthalene tetrachloride. The ligroïn having been distilled off from the filtrate, the liquid residue was mixed with alcoholic potash and precipitated with water; and the oil thus separated, after being dried, was fractionated to constant boiling points. In this manner were obtained monochloronaphthalene and two isomeric dichloronaphthalenes. The distillates which could not be brought to constant boiling points were again treated with chlorine till they partly solidified, then mixed with ligroïn, and the crystalline residue, consisting of dichloronaphthalene tetrachloride, was washed with ligroïn and recrystallised from chloroform. The filtrate freed from ligroïn by distillation yielded heptachlorodinaphthalene. In another experiment the passage of chlorine was continued at a gentle heat till the chlorinated naphthalenes formed on cooling a viscid oil which, when mixed with ligroïn, deposited after a few days, hard crystals of monochloronaphthalene tetrachloride. Another portion of this thick oil was treated with chlorine at a higher temperature till the chlorine passed through unabsorbed, whereby a very viscid oil was produced, which, after washing with ligroïn, was quickly converted into long yellow needles of *β* tetrachloronaphthalene. This body is the final product of the action of chlorine on heated chloronaphthalenes; it does not appear possible to introduce a larger proportion of chlorine, even with aid of iodine. (See, on the contrary, p. 847.)

ADDITIVE-PRODUCTS.—*Naphthalene Tetrachloride*, $C^{10}H^8Cl^4$, crystallises from chloroform in large rhombohedrons, melts at 182°, and is decomposed by boiling with alcoholic potash, yielding a dichloronaphthalene.

Monochloronaphthalene Tetrachloride, $C^{10}H^7Cl.Cl^4$, crystallises from chloroform in clinorhombic prisms melting at 128°–130°; with boiling alcoholic potash it yields trichloronaphthalene.

Dichloronaphthalene Tetrachloride, $C^{10}H^6Cl^2.Cl^4$, crystallises from chloroform in four-sided clinorhombic prisms melting at 172°; converted by boiling alcoholic potash into a tetrachloronaphthalene, and by boiling with nitric acid into dichlorophthalic acid.

It is remarkable that each of these three bodies contains four additive atoms of chlorine. They are nearly inodorous, dissolve sparingly in alcohol, somewhat more easily in ligroïn and in ether, most easily in chloroform. The alcoholic solutions mixed with nitric acid and silver nitrate yield silver chloride on boiling.

SUBSTITUTION-PRODUCTS.—*Monochloronaphthalene*, $C^{10}H^7Cl$, is a colourless, rather mobile oil, boiling at 250°–252°, having a strong odour of naphthalene, and not altered by light. *Monochlorodinitronaphthalene*, $C^{10}H^5Cl(NO^2)^2$, is produced by adding monochloronaphthalene to fuming nitric acid; it forms light yellow soft needles, which may be kneaded together in the hand, and melt at 104°–106°.

Dichloronaphthalene, $C^{10}H^6Cl^2$, exhibits two modifications: *a*. Produced by boiling naphthalene tetrachloride with alcoholic potash. Boils at 280°–282°, and solidifies on cooling to a crystalline mass which melts at 35°–36°. Of the numerous modifications described by Laurent as produced by the process just mentioned (iv. 11), the authors were not able to obtain one: although they crystallised the *a* dichloronaphthalene in three fractions, all three were found to melt at the same temperature.

β Dichloronaphthalene.—The portion of the original chlorinated naphthalenes (see above) which boils between 280° and 285° is a mixture of *a* and *β* dichloronaphthalene, and partly solidifies in the crystalline form after long standing. When these crystals are freed by pressure between bibulous paper from the adhering *a* modification (which in the impure state is an oil), and frequently recrystallised from ether-alcohol, pure *β* dichloronaphthalene is obtained in colourless prisms boiling at 281°–283° (*i.e.* at the same temperature as *a*) and melting at 68°. Th. Hermann (*Ann. Ch. Pharm.* cli. 63) has also obtained this *β* dichloronaphthalene, crystallising in needles and melting at 68°, as one of the products of the action of chlorous acid on naphthalene (p. 858); he also describes two other modifications formed at the same time, one (apparently identical with Laurent's modification *c*) crystallising in acuminated rhombic needles or rhombic laminæ melting at 51°; the other crystallising in strongly nacreous laminæ melting at 92°.

The products formed by treating *a* and *β* dichloronaphthalene with fuming nitric acid are difficult to purify, and therefore not characteristic; but the bromine substitution-products differ somewhat in melting point. *a Tetrachlorotribromodinaphthalene*, $C^{20}H^9Cl^4Br^3$ or perhaps $C^{10}H^5Cl^2Br.C^{10}H^4Cl^2Br^2$, is obtained by dropping 4 at. bromine on 1 mol. of fused dichloronaphthalene, boiling the red solution, after 24 hours, with alcoholic potash, precipitating with water, and recrystallising from ether-alcohol. It forms long soft white needles melting at 74°–76°. *β Tetrachlorotribromodinaphthalene*, $C^{20}H^9Cl^4Br^3$, obtained in the same manner is exactly like the *a* modification in external appearance, but melts at 71°–73°.

Trichloronaphthalene, $C^{10}H^5Cl^3$, obtained by boiling chloronaphthalene tetrachloride with alcoholic potash, crystallises from ether-alcohol in brittle prisms melting at 81°. Its nitro-product is a soft, yellow, crystalline mass.

Heptachlorodinaphthalene, $C^{20}H^9Cl^7 = C^{10}H^5Cl^3 . C^{10}H^4Cl^4$ (?), crystallises from ether-alcohol in very long, yellowish, waxy needles melting at 106°. By prolonged boiling with alcoholic potash it is converted into a product which crystallises from ether-alcohol in colourless six-sided prisms melting at 101°–102°. *Heptachlorodinitrodinaphthalene*, $C^{20}H^7Cl^7(NO^2)^2$ ($= C^{10}Cl^4Cl^3NO^2 . C^{10}H^3Cl^4NO^2$?), crystallises from alcohol in soft yellowish needles melting at 104°–106°.

Tetrachloronaphthalene, $C^{10}H^4Cl^4$, exists also in two isomeric forms: *α*. Produced by boiling dichloronaphthalene tetrachloride with alcoholic potash. Crystallises from ligroïn and ether in soft white needles which melt at 130°. Its nitro-product forms yellow crystalline nodules.—*β*. Forms, as above mentioned, the ultimate product of the action of chlorine gas on heated chloronaphthalenes. It is originally obtained in long yellow needles, but after repeated crystallisation from alcohol, forms soft white needles which melt at 156°–158°. The nitro-product is a soft yellow mass.

All the chloronaphthalenes are easily soluble in ether, ligroïn, and chloroform, less easily in alcohol; they have an odour of naphthalene, weaker as their amount of chlorine is greater, and in the tetrachloronaphthalenes scarcely perceptible. Their nitro-derivatives are mostly soft yellow masses which are difficult to purify, and when heated with aqueous soda or ammonia, are partly converted into a brown-red colouring matter (Faust a. Saame).

Pentachloronaphthalene, $C^{10}H^3Cl^5$, is produced by heating 1 mol. dichloronaphthoquinone with 2 mol. phosphorus pentachloride to 180°–200° in a sealed tube till the yellow crystals disappear:

$$C^{10}H^4Cl^2O^2 + 2PCl^5 = HCl + 2POCl^3 + C^{10}H^3Cl^5.$$

On washing the product with water and dilute soda-ley, and distilling, the pentachloronaphthalene passes over at a temperature above the boiling point of mercury, solidifies in the receiver, and may be obtained in colourless needles by recrystallisation from alcohol. It is insoluble in water, slightly soluble in cold, more freely in hot alcohol, easily soluble in ether. It melts at 108·5°, may be sublimed in needles by cautious heating, and distils unaltered at a higher temperature. It is not attacked by alkalis. It is much less easily oxidable than naphthalene, not being attacked by chromic acid mixture, or by boiling nitric acid of sp. gr. 1·35. By the action of fuming nitric acid, and more easily by heating it in sealed tubes to 180°–200° with nitric acid of sp. gr. 1·15 to 1·2, it is converted into tetrachlorophthalic acid, $C^8H^4Cl^2O^4$ (Graebe, *Ann. Ch. Pharm.* clxix. 8).

Octochloro- or *Perchloro-naphthalene*. $C^{10}Cl^8$.—Berthelot a. Jungfleisch (*Ann. Ch. Phys.* [4] xv. 332) have prepared this compound—first obtained by Laurent (iv. 13)—by treating naphthalene with chlorine, ultimately with addition of antimonic chloride. The product, sublimed and recrystallised from carbon bisulphide, exhibits properties different from those assigned to it by Laurent. It forms splendid crystals belonging to the rhombic system, melts at 135°, and boils with slight decomposition at 403°; 20 c. c. of its solution in carbon bisulphide saturated at 15° contained 5·86 grm. of the compound. Heated with potassium hydrate, it gives off violet vapours (according to Laurent it is not attacked). Heated with hydriodic acid it yields the same products as naphthalene. Its vapour passed, together with hydrogen, through a red-hot tube yields, together with naphthalene, chiefly resinous and coloured products similar to those produced under the same circumstances from naphthalene.

Cyanonaphthalenes. *Monocyano-naphthalene* or *Naphthyl Cyanide*, $C^{10}H^7CN$, is obtained in two modifications, *α* and *β*, by heating the potassium salts of the corresponding naphthyl-sulphurous acids with potassium cyanide:

$$C^{10}H^7.SO^3K + CNK = SO^3K^2 + C^{10}H^7(CN).$$

The *α cyanide* distils over at about 300°, and after a few rectifications forms a colourless liquid having an agreeable odour somewhat like that of bitter almond oil, a sharp burning taste, and solidifying in a few days at ordinary temperatures, quickly and completely at 0°. It may be easily purified by crystallisation from ligroïn, from which it separates in splendid groups of needles having a satiny lustre. It melts constantly at 37·5°, and distils at 297°–298° (corr.).

The *β cyanide* likewise passes over in the first instance at about 300°, as a liquid, but solidifies very quickly at ordinary temperatures. When purified by repeated crystallisation from ligroïn and rectification, it forms a beautiful white mass resembling stearin and melting at 66·5° (*i.e.* 29° higher than the *α* compound) to a colourless or yellowish liquid which solidifies on cooling to a mass of crystalline nodules. It boils constantly at 304°–305° (corr.). Has but a faint odour and a slowly developed burning aromatic taste. It is nearly insoluble in water, but dissolves easily in alcohol and ether, with moderate facility in hot ligroïn, and separates in great part on cooling in groups of white but somewhat indistinct crystals. Better crystals are obtained by leaving solutions of the cyanide in ligroïn or aqueous alcohol to evaporate spontaneously; it then forms thick colourless scales having the aspect of porcelain.

Both α and β naphthyl cyanides are converted by boiling with alcoholic potash into the corresponding naphthoic acids, $C^{11}H^8O^2$ (p. 851). Intermediate compounds are likewise formed having the composition $NH^2(C^{11}H^7O)$ (Merz a. Muhlhäuser, *Zeitschr. f. Chem.* [2] v. 70).

α *Nitrocyanonaphthalene*, $C^{10}H^6(NO^2)(CN)$, obtained by treating α cyanonaphthalene with fuming nitric acid, crystallises from alcohol in yellow needles melting at 81° and solidifying at 74°. It yields by reduction a liquid *amido-base* whose hydrochloride has the composition $C^{10}H^6(CN)NH^2.HCl$. The β *nitro-compound* crystallises from alcohol in yellowish-white laminæ (Welkov, *Deut. chem. Ges. Ber.* 1869, p. 407).

Dicyanonaphthalene, $C^{10}H^6(CN)^2$, is obtained in three modifications by distilling potassium cyanide with the potassium salt: α. Of monobromonaphthyl-sulphurous acid: thin, long, faintly yellow needles, slightly soluble in alcohol and ether, insoluble in water, melting at 204°.—β. Of brominated α naphthyl-sulphurous acid: small yellowish needles, easily soluble in alcohol, melting at 236°.—γ. Of brominated β naphthyl-sulphurous acid: small needles, easily soluble in alcohol, melting at 170°.—δ. From naphthylene-sulphurous acid: yellowish, very slightly soluble in alcohol melting at 262° (Darmstädter a. Wichelhaus, *Zeitschr. f. Chem.* [2] v. 571).

Nitronaphthalenes (Lautemann a. d'Aguiar, *Zeitschr. f. Chem.* [2] i. 564).—Ordinary concentrated nitric acid converts naphthalene only into dinitronaphthalene even after prolonged treatment (Laurent, however, describes two modifications of trinitronaphthalene obtained in this manner, iv. 15). By digesting naphthalene for 12 to 14 days with fuming nitric acid at the boiling heat, a yellow crystalline mixture of di- and tri-nitronaphthalene is obtained; and on mixing the contents of the retort with water, washing the white substance thereby separated with water, drying, treating it with ether, and recrystallising from hot alcohol, trinitronaphthalene, $C^{6}H^{5}(NO^2)^3$, is obtained in monoclinic crystals agreeing perfectly in form with Laurent's β trinitronaphthalene.

Dinitronaphthalene, $C^{10}H^6(NO^2)^2$, which is always obtained in the preceding process as a secondary product, is likewise insoluble in water, but somewhat more soluble than trinitronaphthalene in hot ether or alcohol; it dissolves also in strong nitric acid, hot acetic acid, and turpentine oil, and crystallises therefrom in yellowish needles or in rhombic serrated tables, melting at about 210°. With alcoholic ammonia it forms a white crystalline precipitate, the liquid acquiring a faint rose colour. According to Hollemann (*Zeitschr. f. Chem.* [2] i. 555), yellow dinitronaphthalene may be rendered colourless by treatment with zinc and sulphuric acid at 200°, washing with hot water, and recrystallisation. Darmstädter a. Wichelhaus (*ibid.* v. 253), by exhausting the product of the action of fuming nitric acid on naphthalene with hot alcohol, obtain a dinitronaphthalene which crystallises on cooling in microscopic needles and tables, and when recrystallised from hot chloroform forms four- or six-sided rhombic tables, $\infty P . \infty P\infty . oP$, with angles $\infty P : \infty P = 137°$ and 43°; insoluble in water, dilute nitric acid, and benzol, easily soluble in hot ether and carbon bisulphide, soluble in hot alcohol and chloroform; melting at 170° and resolidifying at 157°–156°. The compound detonates when distilled, dissolves in alcoholic potash with red colour, in sulphuric acid with yellow colour removable by ether. The residue of the treatment with alcohol consists of the modification of dinitronaphthalene previously described. The existence of the second modification of dinitronaphthalene is confirmed by Aguiar (*ibid.* 441), who finds that it possesses the properties described by Darmstädter a. Wichelhaus.

Trinitronaphthalene, $C^{10}H^5Cl^3$, is insoluble in water, only slightly soluble in alcohol and ether; precipitated in flocks from solution in fuming nitric acid. The crystals decrepitate when heated, melt at 214° with partial sublimation, and detonate at a higher temperature. In contact with phosphorus iodide and water it is converted into *naphthenyltriammonium iodide*, $(C^{10}H^5)'''H^6N^3.H^3I^3$, which crystallises from the hot filtrate in needles (Lautemann a. Aguiar). The modification of dinitronaphthalene obtained by Darmstädter a. Wichelhaus yields when treated with fuming nitric acid, a more highly nitrated compound, different from the trinitronaphthalene just described.

Tetranitronaphthalene, $C^{10}H^4(NO^2)^4$, is produced by heating a solution of trinitronaphthalene in fuming nitric acid for four days in closed vessels, and crystallises from hot alcohol in long asbestos-like needles, which melt at 200°, detonate violently at a higher temperature, and are coloured deep red by alcoholic ammonia. By excess of phosphorus iodide and water it is converted into *naphthenylene-tetrammonium iodide*, $(C^{10}H^4)^{iv}H^8N^4.4HI$, which crystallises in yellowish laminæ easily soluble in alcohol (Lautemann a. d'Aguiar).

Diazonaphthalene. $C^{10}H^6N^2$.—The nitrate of this base, $C^{10}H^6N^2.HNO^3$, is formed by the action of nitrous acid on moistened nitrate of naphthylamine, and is obtained, on filtering the solution from a brown-red amorphous product, and leaving it to evaporate, in white, easily soluble, explosive needles. Its aqueous solution is decomposed at the boiling heat, with evolution of nitrogen and formation of naphthol (v. 856):

$$C^{10}H^6N^2.HNO^3 + H^2O = C^{10}H^8O + HNO^3 + N^2.$$

Diazonaphthalene perbromide, $C^{10}H^6N^2.HBr^3$, forms orange-red crystals; the *platinochloride*, $2(C^{10}H^6N^2.HCl).PtCl^4$, forms short, yellowish, nearly insoluble prisms. *Diazonaphthalimide*, $C^{10}H^6N^2.NH$, passes over as a yellowish oil, when the substance obtained by the action of ammonia on the perbromide is distilled with water (Griess, *Jahresb.* 1866, p. 459). All these reactions are analogous to those of diazobenzene (iv. 430).

Diazoamidonaphthalene, $C^{20}H^{15}N^3 = C^{10}H^6N^2.C^{10}H^7(NH^2)$, analogous to diazoamidobenzene (iv. 459), is formed by the action of nitrous acid on a well-cooled solution of naphthylamine:

$$2C^{10}H^9N + HNO^2 = 2H^2O + C^{20}H^{15}N^3;$$

or by precipitating diazonaphthalene hydrochloride with a solution of naphthylamine, or better by the action of a slightly alkaline solution of sodium nitrite on crystallised neutral naphthylamine hydrochloride. It separates from alcohol in yellow-brown laminæ which melt at 100°, and decompose with explosion at higher temperatures. When heated, even with the weakest acids, it splits up into naphthylamine and naphthol; with concentrated mineral acids it acquires a transient violet colour (C. A. Martius, *Zeitschr. f. Chem.* [2] ii. 137).

Azodinaphthyldiamine, $\left.\begin{matrix}(C^{10}H^7)^2\\ N'''\\ H\end{matrix}\right\}N^3$ (iv. 23), isomeric with the preceding, is formed, together with naphthol, by the action of nitrous acid on warm alcoholic solutions of naphthylamine; also by treating that base with sodium stannate:

$$3C^{10}H^9N + O^3 = C^{20}H^{15}N^3 + C^{10}H^8O + 2H^2O.$$

It forms tolerably stable salts, whose solutions are violet, and crystallises from alcohol in long reddish-yellow needles which melt at 136°, solidify at 125°, and distil almost without decomposition.

Azodinaphthyldiamine is also formed by the action of strong sulphuric acid and of other acids, except hydrochloric acid, on naphthylamine (Chapman, *Chem. Soc. J.* [2] iv. 329). On its formation by the action of nitrous acid on naphthylamine, see also Chapman (*ibid.* 135).

Ethyl-naphthalene, $C^{12}H^{12} = C^{10}H^7(C^2H^5)$, is produced, similarly to ethylbenzene (p. 292), by the action of sodium in excess on a cooled mixture of monobromonaphthalene and ethyl bromide in presence of ether. On distilling off the ether, and subjecting the liquid which passes over at a higher temperature to fractional distillation, it separates into naphthalene and ethyl-naphthalene. The latter is a colourless liquid having a faint odour, boiling at 250°, and of about the same specific gravity as water (Fittig a. Remsen, *Zeitschr. f. Chem.* [2] v. 37).

Methyl-naphthalene, $C^{11}H^{10} = C^{10}H^7(CH^3)$, is produced in like manner from bromonaphthalene and methyl iodide. The product is a colourless liquid, boiling constantly at 231°–232°, having a sp. gr. of 1·027 at 11·5°, and remaining liquid at −18° (Fittig). Stacewicz (*ibid.* 182), by heating the lead salt of naphthyl-sulphurous acid with calcium acetate and quick lime, distilling, and crystallising from alcohol, obtained a small quantity of yellowish laminæ, having nearly the composition of methyl-naphthalene. The reaction appears to be:

$$\begin{gathered}(C^{10}H^7SO^3)^2Pb + (C^2H^3O^2)^2Ca + 2CaO = 2C^{10}H^7(CH^3) + \\ SO^3Pb + SO^3Ca + 2CO^3Ca.\end{gathered}$$

NAPHTHALENE ALCOHOL. $C^{10}H^{12}O^4 = \left.\begin{matrix}(C^{10}H^8)^{iv}\\ H^4\end{matrix}\right\}O^4$ (Neuhoff, *Ann. Ch. Pharm.* cxxxvi. 342).—A tetratomic alcohol produced from the corresponding chlorhydrin by decomposition with alkalis:

$$C^{10}H^8Cl^2(OH)^2 + 2KOH = 2KCl + C^{10}H^8(OH)^4.$$

The chlorhydrin is obtained by treating finely pulverised naphthalene with excess of moderately concentrated hypochlorous acid, and agitating the liquid (filtered after 24 hours, freed from dissolved mercury by hydrogen sulphide, and saturated with common salt) with ether. On distilling off the ether, and drying the residue in rarefied air, *naphthalene chlorhydrin* remains as a light yellow body, crystallising in well-defined prisms, slightly soluble in water, easily soluble in alcohol, quickly turning brown in the air, melting at a gentle heat, and decomposing at a higher temperature.

To prepare the *alcohol*, the alcoholic or aqueous solution of the chlorhydrin is heated for a few hours with 3 or 4 mol. potassium hydrate, and the dilute solution, acidulated with hydrochloric acid and mixed with common salt, is agitated with ether. On evaporating the ether (and decolorising if necessary in alcoholic solution with animal charcoal) the naphthalene alcohol crystallises in prisms which rapidly turn brown. It melts at a gentle heat, decomposes when distilled, is slightly soluble in water, easily in alcohol and ether, and with brown colour in aqueous potash. The alcoholic solution mixed with a little ammonia, forms with salts of lead, silver, and other metals, precipitates which acquire a darker colour when exposed to light. The lead compound, $C^{10}H^8Pb^2O^4$, absorbs carbon dioxide from the air, and when decomposed by hydrochloric acid, yields the alcohol in its original state. The solution of the alcohol in strong sulphuric acid is brown, and contains an acid whose barium, calcium, and lead salts are easily soluble in water. The calcium salt, $\left.\begin{matrix}(SO^2)^2\\ C^{10}H^8\\ H^2Ca\end{matrix}\right\}O^6$, crystallises in tufts of prisms. Glacial acetic acid decomposes the alcohol, forming a black resin and a red body soluble in ether. The solution of the alcohol in warm very dilute nitric acid leaves on evaporation yellow prisms of naphthoxalic acid, $C^{10}H^8O^6$. The alcohol or the chlorhydrin heated for some time with concentrated hydriodic acid, forms a mobile liquid distillable with water, and probably consisting of cymene holding naphthalene in solution.

NAPHTHALENE-RED. See NAPHTHYLAMINE (p. 861).

NAPHTHENYL-AMMONIUMS. See page 848.

NAPHTHOCYAMIC ACID. $C^{28}H^{18}N^8O^9$ (Mühlhäuser, *Ann. Ch. Pharm.* cxli. 214).—Produced by the action of potassium cyanide on dinitro-naphthalene:

$$2C^{10}H^6(NO^2)^2 + 12CNH + 9H^2O = C^{28}H^{18}N^8O^9 + 4CO^2 + 8NH^3.$$

The potassium salt is prepared by agitating a mixture of 3 pts. pulverised dinitronaphthalene in 38 pts. alcohol with a solution of 6 pts. potassium cyanide in 57 pts. water till a brown-red colour is produced, and then heating the liquid to the boiling point till it assumes a fine blue-green colour. The solution decanted while still hot gradually deposits the impure potassium salt, which may be purified by washing with cold water (till the water runs away blue), solution in hot water, repeated precipitation with concentrated potassium carbonate, and treatment with hot ether after drying over sulphuric acid. It contains $C^{28}H^{17}N^8O^9K + H^2O$, and forms a dark mass having a strong coppery lustre, especially after friction; insoluble in ether, but dissolving easily, and with fine blue colour, in hot water and in alcohol. When heated it detonates with a reddish light, giving off a peculiar aromatic odour, and leaving a bulky charcoal. The *ammonium salt*, formed by decomposing the potassium salt with strong solution of sal-ammoniac, is a crystalline precipitate soluble in hot water and in alcohol. The *barium salt*, $C^{28}H^{16}N^8O^9Ba$ (?), is a dark blue precipitate having a coppery lustre when dry, detonating when heated like the potassium salt. The *silver salt*, $C^{28}H^{16}N^8O^9Ag^2$, is insoluble in water, has a lustre of bronze, and detonates with great violence when heated. The blue solution of the potassium salt mixed with the smallest quantity of any free acid becomes greenish, and on further acidulation, greenish-yellow, depositing naphthocyamic acid, $C^{28}H^{18}N^8O^9$, as a dark brown precipitate, forming when dry a black shining mass. It is insoluble in ether, nearly insoluble in water, more easily in alcohol, still more in amylic alcohol, forming a dark brown-red liquid. Its solution turns green or blue when mixed with a small quantity of a base.

Wislicenus (*ibid.* vi. 159) points out that the acid in question yields by oxidation, not glyceric, but (as first product) carbacetoxylic acid; that it is not converted into glycerin by nascent hydrogen; and when treated with hydriodic acid is easily transformed into β-iodopropionic acid. Sarcolactic acid appears to be a mixture of two acids, inasmuch as its zinc salt may be separated, by treatment with strong alcohol, into a sparingly soluble crystalline salt and an easily soluble amorphous salt. The acid of the latter appears to be identical with paralactic or β-oxypropionic acid; but that of the crystalline zinc salt is not identical with ordinary lactic acid, inasmuch as it exerts a strong dextrorotatory action on polarised light, whereas both ordinary lactic and paralactic acids are optically inactive. See further Heintz, *Ann. Ch. Pharm.* clvii. 291, 295;—Erlenmeyer, *ibid.* clviii. 262; also *Chem. Soc. J.* [2] ix. 361, 546.

Reactions.—1. Paralactic acid oxidised with *potassium dichromate*, or with dilute *nitric acid*, or by fusion with *potash*, is converted into malonic acid, $C^3H^4O^4$; but ordinary lactic acid treated with sulphuric acid and potassium dichromate, is converted into formic and acetic acids (Dossios, *Jahresb.* 1866, p. 384):

$$\underset{\text{Paralactic.}}{\left\{\begin{matrix}CH^2OH\\CH^2\\COOH\end{matrix}\right.} + O^2 = H^2O + \underset{\text{Malonic.}}{\left\{\begin{matrix}COOH\\CH^2\\COOH\end{matrix}\right.}$$

$$\underset{\text{Lactic.}}{\left\{\begin{matrix}CH^3\\CHOH\\COOH\end{matrix}\right.} + O = \underset{\text{Formic.}}{\left\{\begin{matrix}H\\COOH\end{matrix}\right.} + \underset{\text{Acetic.}}{\left\{\begin{matrix}CH^3\\COOH\end{matrix}\right.}$$

According to Chapman and Smith (p. 152), the products are acetic acid, carbon dioxide, and water: $C^3H^6O^3 + O^3 = C^2H^4O^2 + CO^2 + H^2O$.

2. Ordinary lactic acid heated for several hours to 130° with dilute *sulphuric acid* is converted into aldehyde and formic acid:

$$\underset{\text{Lactic acid.}}{\left\{\begin{matrix}CH^3\\CHOH\\COOH\end{matrix}\right.} + HOH = \underset{\text{Ethylidene glycol.}}{\left\{\begin{matrix}CH^3\\CHOH\\OH\end{matrix}\right.} + \underset{\text{Formic acid.}}{\left\{\begin{matrix}H\\COOH\end{matrix}\right.}$$

$$\underset{\text{Ethylidene glycol.}}{\left\{\begin{matrix}CH^3\\CHOH\\OH\end{matrix}\right.} = \underset{\text{Aldehyde.}}{\left\{\begin{matrix}CH^3\\CHO\end{matrix}\right.} + H^2O$$

Paralactic acid similarly treated would probably be resolved into formic acid and ethylene glycol (Erlenmeyer, *Zeitschr. f. Chem.* [2] iv. 343).

3. Lactic acid mixed with *cupric sulphate* forms a deep blue liquid without precipitation, whereas paralactic acid is almost completely precipitated (Dossios, *loc. cit.*).

4. Lactic acid heated to 160°–180° in a stream of gaseous *hydrobromic acid*, or to 100° in sealed tubes with saturated aqueous hydrobromic acid, is converted into bromopropionic acid, $C^3H^5BrO^2$ (Kekulé, *Ann. Ch. Pharm.* cxxx. 11).

5. An ethereal solution of lactic acid treated with *bromine* in a well-cooled vessel, and afterwards heated to 100° in a retort with upright condenser, yields a liquid from which water throws down a gradually crystallising oil, while ordinary lactic acid remains dissolved. The crystalline product, which contains about 6·8 p. c. bromine, is neutral, melts at 83°–85°, dissolves easily in ether, separating therefrom in large acute rhombic prisms, and is decomposed by silver oxide and acetate, also by sodium-amalgam, yielding products not yet examined (Wichelhaus, *Jahresb.* 1867, p. 402).

According to Claus (*Ann. Ch. Pharm.* cxxxvi. 287), calcium lactate yields by dry distillation, acrylic acid, phenol, and a fetid oil varying in boiling point from 75° to 210°. Potassium lactate subjected to electrolysis yields large quantities of carbon dioxide and aldehyde-resin (Brester, *Jahresb.* 1866, p. 87). Ethyl lactate is converted by phosphorus trichloride into ethyl chloropropionate (Frankland a. Duppa, *ibid.* 1865, p. 386):

$$3C^3H^5(C^2H^5)O^3 + PCl^3 = PH^3O^3 + 3C^3H^4Cl(C^2H^5)O^2.$$

Dibromolactic acid, $C^3H^4Br^2O^3$, is formed by enclosing 1 mol. pyroracemic acid, $C^3H^4O^3$ (dried by standing over oil of vitriol and quick lime), with 1 mol. bromine in a sealed tube, and leaving the tube for several hours in ice-cold water. A viscid product containing capillary crystals is then formed, and the colour of the bromine disappears, without perceptible formation of hydrobromic acid. The product quickly absorbs moisture from the air, and decomposes with evolution of hydrobromic acid; it manner with naphthylamine, is insoluble in water and benzol, slightly soluble in alcohol, and melts at 244° (Hofmann).

Naphthoic Anhydride, $(C^{11}H^7O)^2O$, obtained by distilling calcium naphthoate with naphthoic chloride, washing the distillate with water and alcohol, and crystallising from boiling benzol, forms prisms melting at 145°, insoluble in water, slightly soluble in alcohol, easily soluble in ether and in benzol (Hofmann).

Oxynaphthoic Acid. $C^{11}H^8O^3 = C^{10}H^6(OH).COOH$. *Carbonaphtholic Acid* (Eller, *Ann. Ch. Pharm.* clii. 277).—This acid, related to naphthol in the same manner as salicylic acid to phenol, is formed by passing dry carbon dioxide over an intimate mixture of 1 mol. naphthol and 2 at. sodium, the reaction being completed at the heat of the water-bath. The mass is then exposed to the air for a short time, to oxidise the remaining sodium, the sodium oxynaphthoate is dissolved in water, and the solution mixed with hydrochloric acid. The oxynaphthoic acid, which is almost insoluble in water, is then precipitated in yellowish flocks which may be recrystallised from alcohol and ether. It forms colourless needles easily soluble in alcohol and ether, and precipitated therefrom by water; it has an acid reaction, and melts at 186° to 188°, turning brown at the same time. The *potassium salt* forms slightly soluble needles. The *copper salt* is a green, the *lead salt* a white sparingly soluble precipitate; the *silver salt* a curdy precipitate. Ferric chloride produces with the acid a strong blue colour; ferrous sulphate, after a while, a blue-red colour. Barium chloride forms no precipitate.

The oxynaphthoic acid above described was prepared with a mixture of α and β naphthol. Schäffer, however (*Ann. Ch. Pharm.* clii. 291), has prepared α oxynaphthoic acid from pure α naphthol, and finds that it agrees in every respect with the acid obtained by Eller; melting point 185°–186°. Hence it appears that a mixture of α and β naphthol treated with sodium and carbon dioxide yields only α oxynaphthoic acid. Schäffer finds indeed that β naphthol treated in the same manner is but very slowly attacked, yielding only small quantities of the corresponding oxynaphthoic acid. This β acid is very much like the α acid, and forms similar precipitates with lead, copper, and silver salts. With ferric chloride, however, it produces, not a blue, but an inky-violet colour. α Oxynaphthoic acid heated to 120°–130° in sealed tubes with hydriodic acid, is reduced to α naphthol, just as salicylic acid is reduced to phenol (Schäffer).

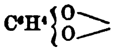
Naphthyl-bicarboxylic, *Bicarbonaphthalic*, or *Naphthophthalic Acid*, $C^{12}H^8O^4 = C^{10}H^6.(CO^2H)^2$, is easily produced by boiling dicyanonaphthalene with strong potash-ley, and precipitating the resulting potassium salt with hydrochloric acid:

$$C^{10}H^6(CN)^2 + 4H^2O = 2NH^3 + C^{10}H^6.(CO^2H)^2.$$

It is very slightly soluble in hot water, and is precipitated from alcoholic solution by water in nearly colourless microscopic needles, which do not melt at 240°. Its neutral barium salt, $C^{10}H^6.(CO^2)^2Ba + 2H^2O$, is very easily soluble, and its solution gives with ferric chloride a light yellow ferric salt nearly insoluble in hot water—also a copper salt separating in groups of green needles—and sparingly soluble lead and silver salts. The alcoholic solution of the acid poured into water, exhibits a fluorescence very much like that of quinine solutions (Darmstädter a. Wichelhaus, *Deut. chem. Ges. Ber.* 1869, p. 356).

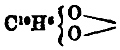
NAPHTHOL. See NAPHTHYL ALCOHOL.

NAPHTHOQUINONE. $C^{10}H^6O^2$ (Graebe, *Ann. Ch. Pharm.* cxlix. 1; *Zeitschr. f. Chem.* [2] iv. 114; v. 563; *Jahresb.* 1868, p. 471. Th. Hermann, *Ann. Ch. Pharm.* cli. 63; *Jahresb.* 1868, p. 390).—This compound is derived from naphthalene by substitution of the diatomic group (O—O)″ for H^2, being related to naphthalene in the same manner as ordinary quinone to benzene:



$$C^6H^4\left\{\begin{matrix}O\\O\end{matrix}\right.\!\!>$$

Quinone.



$$C^{10}H^6\left\{\begin{matrix}O\\O\end{matrix}\right.\!\!>$$

Naphthoquinone.

Naphthoquinone is obtained by subjecting the potassium salt of chloronaphthosulphoquinonic acid—one of the products of the action of potassium chlorate and sulphuric acid on naphthalene (p. 854)—to dry distillation. Sulphurous anhydride is then evolved, together with yellow-red vapours which quickly condense, and on treating this distillate, or the residual charcoal, with ether, golden-yellow solutions are obtained. These solutions, when left to evaporate, deposit yellow or red flocks, which when dried and heated between watch-glasses, yield naphthoquinone as a yellow sublimate consisting of soft laminæ.

Naphthoquinone dissolves sparingly in alcohol and ether, forming golden-yellow solutions which exhibit a beautiful green fluorescence. The solutions mixed with ammonia reduce silver nitrate at the boiling heat. They are slowly decomposed by zinc and hydrochloric acid. With alcoholic potash, naphthoquinone forms a dark-coloured solution; in strong sulphuric acid, it dissolves with fine purple colour, and is precipitated apparently unaltered on dilution with water. By boiling with strong nitric acid in presence of silver, it is oxidised, the solution on cooling depositing shining rhombic laminæ, which exhibit the characters of silver phthalate (Hermann).

The four oxychlorinated derivatives of naphthalene described by Laurent, two of which are acids, and the two others the corresponding chlorides (see OXYNAPHTHALIC ACID (iv. 313), may be regarded as derivatives of naphthoquinone; thus:

Chloroxynaphthyl Chloride = Dichloronaphthoquinone . . . $C^{10}H^4Cl^2\begin{cases}O\\O\end{cases}\!\!>$

Perchloroxynaphthyl Chloride = Hexchloronaphthoquinone . . $C^{10}Cl^6\begin{cases}O\\O\end{cases}\!\!>$

Chloroxynaphthalic acid = Chloroxynaphthoquinone . . $C^{10}H^4Cl(OH)\begin{cases}O\\O\end{cases}\!\!>$

Perchloroxynaphthalic acid = Pentachloroxynaphthoquinone $C^{10}Cl^5(OH)\begin{cases}O\\O\end{cases}\!\!>$

To the last of these is related the acid $C^{10}H^6O^3$, discovered by Martius a. Griess (p. 857), which has the constitution of oxynaphthoquinone, $C^{10}H^5(OH)\begin{cases}O\\O\end{cases}\!\!>$ (Graebe).

Dichloronaphthoquinone, $C^{10}H^4Cl^2(O^2)''$, may be prepared by gradually adding a mixture of naphthalene-yellow (a commercial sodium or potassium salt of dinitronaphthol, p. 856) with 3 or 4 pts. of potassium chlorate to crude hydrochloric acid diluted with an equal volume of water. The mixture is warmed, and as soon as all the naphthalene-yellow has been introduced, more potassium chlorate is added by successive portions till the yellow-red oil at first produced is converted into yellow crystals. These washed on a filter with hot water, freed from oily mixtures by treatment with cold alcohol, and recrystallised from hot alcohol, yield dichloronaphthoquinone in golden-yellow needles, or more rarely in laminæ. It is insoluble in water, slightly in cold alcohol or ether, moderately soluble in hot alcohol; is but slowly attacked by cold soda-ley, but dissolves at the boiling heat, with crimson colour, producing sodium chloroxynaphthalate. It melts at 189°, but begins to sublime below that temperature in long yellow needles, sometimes also in laminæ. Heated in a sealed tube with phosphorus pentachloride, it is converted into pentachloronaphthalene:

$$C^{10}H^4Cl^2O^2 + 2PCl^5 = HCl + 2POCl^3 + C^{10}H^3Cl^5.$$

Chloroxynaphthoquinone, $C^{10}H^4Cl(OH)(O^2)''$, produced by the action of alkalis on dichloronaphthoquinone, is identical with the chloroxynaphthalic acid obtained in like manner by Laurent (iv. 14), and by P. and E. Depouilly (*Bull. Soc. Chim.* [2] iv. 10). On treating the dichloronaphthoquinone with a little alcohol, and adding caustic potash, the liquid solidifies to a mass of cherry-red needles, and by treating the product with hydrochloric acid, the chloroxynaphthalic acid is separated as a yellow precipitate melting at 200°, and subliming in needles. It is slightly soluble in cold water, more easily in boiling water, also in alcohol, ether, and benzol. It dissolves in strong sulphuric acid, and is precipitated therefrom by water. Its *potassium salt* forms cherry-red needles easily soluble in hot, slightly in cold water. The *barium salt*, obtained by precipitation, separates from hot-saturated aqueous solutions in yellow silky needles, $(C^{10}H^4ClO^3)^2Ba + H^2O$, which give up their water of crystallisation at 100°. The *calcium salt*, obtained in like manner, forms yellow needles, more soluble than the barium salt. The *lead* and *silver salts* are cherry-red precipitates.

Chloroxynaphthalic acid heated in sealed tubes with 3 mol. phosphorus pentachloride, yields pentachloronaphthalene, phosphorus oxychloride, and hydrochloric acid. Treated in aqueous or alcoholic solution with sodium-amalgam, it yields a number of reduction-products, which were observed some years ago by Strecker (*Ann. Ch. Pharm.* lxxv. 17), but have not been examined. Its potassium salt when heated yields phthalic anhydride, together with potassium chloride and carbon:

$$C^{10}H^4Cl(OK)O^2 = KCl + C^2 + C^8H^4O^3.$$

Sulpho-acids derived from Naphthoquinone.—Dichloronaphthoquinone dissolves at a gentle heat in acid potassium sulphite, and the solution on cooling deposits the potassium salt, $C^{10}H^4\begin{cases}OH\\O.SO^2K\\(SO^3K)^2\end{cases} + 2H^2O$, in yellowish octohedrons, becoming pure and colourless by recrystallisation. This salt gives off 1 mol. water at 100°, dissolves very easily in water, but is insoluble in alcohol. Its formation is represented by the equation:

$$C^{10}H^4Cl^2O^2 + 3HSO^3K = 2HCl + C^{10}H^4\begin{cases}OH\\ O.SO^3K\\ (SO^3K)^2.\end{cases}$$

The sodium salt obtained in like manner contains $3H^2O$, is more soluble in water, and crystallises in hard ill-defined tables. Both salts decompose when heated above 100°.

The potassium salt is converted by potash-ley into *potassium oxynaphthosulphoquinonate*:

$$C^{10}H^4\begin{cases}OH\\ O.SO^3K\\ (SO^3K)^2\end{cases} + KOH = 2HSO^3K + C^{10}H^4\begin{cases}O^2\\ OK\\ SO^3K.\end{cases}$$

The yellow-red precipitate thus obtained is very soluble in water, and therefore difficult to separate from the excess of caustic potash and from the acid potassium sulphite. It is but slightly soluble in the strong alkaline liquid, insoluble in alcohol. By cooling the hot-saturated aqueous solution, it is obtained in yellow-red, microscopic, sickle-shaped needles. Barium chloride forms in the solution a yellow precipitate slightly soluble in water. The calcium precipitate is somewhat more soluble. Lead acetate forms a yellow precipitate insoluble in water. With tin and hydrochloric acid a colourless hydro-compound is obtained (Graebe).

Chloronaphthosulphoquinonic acid, $C^{10}H^5ClSO^6$, is formed as a potassium salt amongst the products of the reaction of potassium chlorate and sulphuric acid on naphthalene (pp. 844, 858). When the dark brown liquid remaining after repeatedly exhausting this product with ether, and containing sulphuric acid and acid potassium sulphate, is left to stand in the concentrated state, it gradually deposits potassium chloronaphthosulphoquinonate in brown crystalline crusts. These are washed, dried on bibulous paper, and freed from acid potassium sulphate by means of water or dilute alcohol. If the residue be then dissolved by boiling with water, and the solution filtered and evaporated, brown indistinctly crystalline masses are obtained, consisting of potassium chloronaphthosulphoquinonate, $C^{10}H^4KClSO^6 = C^{10}H^4\begin{cases}Cl\\ (O^2)''\\ SO^4K\end{cases}$.

This salt is sparingly soluble in water and alcohol, insoluble in ether. The aqueous solution has an acid reaction, a deep red-brown colour, and is easily decolorised by zinc and hydrochloric acid. A fragment of the salt held in a flame swells up with vermicular excrescences. The solution dyes silk a fine reddish colour, is not precipitated by metallic salts, but reduces silver after addition of ammonia (Hermann).

When the action of potassium chlorate and sulphuric acid on naphthalene is completed, not by heating, but by leaving the mixture for a considerable time and frequently agitating, the liquid retains its yellow-red colour, and becomes dark brown only after dilution with water. In this case the potassium salt of the sulpho-acid, though obtained in a perfectly analogous way, has the composition $C^{20}H^9K^2Cl^3S^2O^{12}$. It resembles the former sulpho-salt, but yields a lighter-coloured powder, and is somewhat more soluble in alcohol and ether (Hermann).

The first sulpho-acid is perhaps formed as follows: By the action of chlorous anhydride on naphthalene, dichloroxynaphthol is first produced:

$$C^{10}H^8 + Cl^2O^3 = H^2O + C^{10}H^6Cl^2O^2;$$

this by further oxidation is converted into dichloronaphthoquinone, with simultaneous formation of dichloronaphthalene:

$$2C^{10}H^6Cl^2O^2 + C^{10}H^8 + Cl^2O^3 = 3H^2O + C^{10}H^6Cl^2 + 2C^{10}H^4Cl^2O^2;$$

and the dichloronaphthoquinone reacts with the acid potassium sulphate, in such a manner as to form the potassium salt of the first of the above-described sulpho-acids:

$$C^{10}H^4Cl^2O^2 + SO^4HK = HCl + C^{10}H^4Cl(SO^4K)O^2.$$

The formation of the second sulpho-acid may be represented by the equation:

$$2C^{10}H^4Cl^2O^2 + 2SO^4HK = HCl + C^{20}H^9Cl^3(SO^4K)^2O^4.$$

The following compounds belonging to the naphthoquinone group have recently been obtained by Graebe a. Ludwig (*Ann. Ch. Pharm.* June 1870):

Diamido-naphthol	$C^{10}H^5(OH)\left\{\begin{matrix}NH^2\\NH^2\end{matrix}\right.$
Di-imido-naphthol	$C^{10}H^5(OH)\left\{\begin{matrix}HN\\HN\end{matrix}\right>$
Amido-oxynaphthol	$C^{10}H^5(OH)\left\{\begin{matrix}NH^2\\OH\end{matrix}\right.$
Oxynaphtho-quinone or Naphtholic acid	$C^{10}H^5(OH)\left\{\begin{matrix}O\\O\end{matrix}\right>$

NAPHTHOXALIC ACID. $C^{10}H^8O^6$.—This acid, isomeric if not identical with dioxynaphthalic acid (p. 850), remains, on evaporating a solution of naphthalene alcohol (p. 850) in warm very dilute nitric acid, in yellowish prisms easily soluble in water and in alcohol. It sublimes when heated above 100° in monoclinic prisms, and forms easily soluble crystallisable salts with baryta and ammonia. The *silver salt*, $C^{10}H^6Ag^2O^6$, and the lead salt, are amorphous light yellow precipitates (Neuhoff, *Ann. Ch. Pharm.* cxxxvi. 342).

NAPHTHYL or *Dinaphthyl.* $C^{20}H^{14} = C^{10}H^7.C^{10}H^7$ (Lossen, *Ann. Ch. Pharm.* cxliv. 71; *Jahresb.* 1867, p. 711).—This hydrocarbon is obtained, together with other products, by heating naphthalene with a mixture of manganese dioxide and sulphuric acid diluted with twice its weight of water. Carbon dioxide is then evolved; the acid liquid deposits phthalic acid together with manganous sulphate; and the viscid undissolved mass contains dinaphthyl together with a red resin:

$$2C^{10}H^8 + O = H^2O + C^{20}H^{14}.$$

On repeatedly exhausting the brown-red mass with hot alcohol, and leaving the united reddish-yellow extracts to cool, the red resin first separates, and then the dinaphthyl, in yellow nodules. After repeated crystallisation from alcohol, with addition of animal charcoal, it forms faintly yellow nacreous scales, which become colourless by sublimation. From ether, in which it is much more soluble, it crystallises in moss-like aggregates; from ether-alcohol in perfectly developed octohedrons. It dissolves very easily in carbon bisulphide, and crystallises from benzol in the same form as from alcohol. It melts at 154°, and boils at a temperature above the boiling point of mercury.

Dibromodinaphthyl, $C^{20}H^{12}Br^2$, is most easily prepared by allowing the vapour of a weighed quantity of bromine to be absorbed by dinaphthyl spread upon a glass plate placed under a bell jar, a little water being also present to absorb the hydrobromic acid formed. The product is treated with boiling alcohol, and the residual white powder is dissolved in hot benzol. It crystallises in thin monoclinic prisms, volatile without decomposition, melting at 215°, nearly insoluble in alcohol, somewhat more soluble in ether, easily in boiling benzol and carbon bisulphide. It is not altered by alcoholic solutions of potash, potassium cyanide, ammonia, potassium acetate, or silver acetate, even at the boiling heat. It dissolves in fuming nitric acid, forming a nitro-compound precipitable by water.

Hexbromodinaphthyl, $C^{20}H^8Br^6$, is formed by treating dinaphthyl with excess of bromine, and remains on evaporating its solution in carbon bisulphide (previously agitated with soda-ley) as a yellow resinous mass. It dissolves in alcohol, and is for the most part precipitated therefrom by water as a yellow powder. By agitating its solution in aqueous ether-alcohol with sodium-amalgam, it is converted into dinaphthyl.

Hexchlorodinaphthyl, $C^{20}H^8Cl^6$, obtained by saturating a solution of dinaphthyl in carbon bisulphide with chlorine, and purified by agitation with soda-ley and water, is a yellow, resinous, easily fusible mass, which is decomposed by heat, and likewise reduced to dinaphthyl by sodium-amalgam.

Tetranitrodinaphthyl, $C^{20}H^{10}(NO^2)^4$, is formed by adding dinaphthyl to fuming nitric acid, and separates, on mixing the solution with water, in yellow flocks, which are deposited from solution in hot alcohol as an orange-coloured powder made up of resinous spherules. It melts and detonates when heated, and when treated in alcoholic solution with tin and hydrochloric acid, yields a small quantity of a very unstable base, the salts of which acquire a transient blue or violet colour by the action of potassium chromate.

NAPHTHYL ALCOHOL or **NAPHTHOL.** $C^{10}H^8O = C^{10}H^7(OH)$ (Eller, *Zeitschr. f. Chem.* [2] iv. 723; Maikopar, *ibid.* v. 215; Schäffer, *ibid.* 395).—Of this alcohol there are two modifications, α and β, produced by fusing the lead or potassium salts of the corresponding naphthylsulphurous acids with excess of potash. At the end of the reaction, the fused mass is dissolved in water, the filtered solution is mixed with hydrochloric acid, and the separated naphthol, after recrystallisation from water, is further purified by sublimation. α Naphthol likewise distils over easily with vapour of water, but β naphthol cannot be separated in this manner from the fused mass.

α Naphthol crystallises in small white shining needles, sometimes also in laminæ, easily soluble in alcohol, ether, chloroform, and benzene, sparingly soluble in hot, nearly insoluble in cold water. It has a faint odour, like that of phenol, and its vapour excites sneezing. The aqueous solution mixed with chloride of lime assumes a deep violet colour, changing when heated to red-brown, with separation of brown flocks. A deal-shaving dipped into the aqueous solution, then wetted with hydrochloric acid and exposed to the sun, acquires a peculiar green colour, gradually changing to red-brown; the same changes of colour are produced more slowly in diffused daylight. α Naphthol melts at 94° (Schäffer); at 96° and sublimes in needles (Maikopar). It is identical with the naphthol which Griess obtained from diazonaphthalene (v. 1093). β Naphthol is easily soluble in alcohol, ether, chloroform, and benzene, sparingly soluble in hot water, and crystallises therefrom in laminæ. Its aqueous solution is coloured yellow by chloride of lime, and deposits yellow flocks when warmed. A deal-shaving moistened with hydrochloric acid is coloured by it nearly in the same manner as by α naphthol, but much more quickly (Schäffer). It melts at 122° (Schäffer); at 123° and sublimes in laminæ (Maikopar). A mixture of α and β naphthol melts at a lower temperature than either of the naphthols separately (Maikopar).

Naphthol heated with *potassium* or *sodium*, or with *hydrate of potassium, sodium*, or *barium*, unites therewith like phenol, but the compounds formed are less soluble than the phenol-compounds, being decomposed, with separation of naphthol, when evaporated over the water-bath or when carbonic acid is passed through them.

Naphthol heated in the water-bath with an equivalent quantity *of phosphorus pentachloride* yields trinaphthylic phosphate, $PO^4(C^{10}H^7)^3$, in compact crystalline masses, the α ether thus produced melting at 145°, the β ether at 108°. A small quantity of an oily chlorinated compound is also formed, probably naphthyl chloride (Schäffer).

Dinitronaphthol. $C^{10}H^6(NO^2)^2O$ (Martius, *Berl. Akad. Ber.* 1867, p. 519; *Zeitschr. f. Chem.* [2] iv. 80. Darmstädter a. Wichelhaus, *Ann. Ch. Pharm.* clii. 298). —This compound is not produced—at least in any available quantity—by direct nitration of free naphthol; but it may be prepared by the action of nitric acid upon naphthol in the nascent state, namely by treating a dilute solution of naphthylamine hydrochloride with potassium nitrite, whereby diazonaphthalene hydrochloride is produced, and boiling this solution with nitric acid. The diazonaphthalene then splits up into nitrogen and naphthol, which latter is immediately converted into the dinitro-compound by the nitric acid present:

$$\underset{\substack{\text{Naphthylamine}\\ \text{hydrochloride.}}}{C^{10}H^9N.HCl} + \underset{\substack{\text{Nitrous}\\ \text{acid.}}}{NHO^2} = 2H^2O + \underset{\substack{\text{Diazonaphthalene}\\ \text{hydrochloride.}}}{C^{10}H^6N^2.HCl}$$

$$\underset{\substack{\text{Diazonaphthalene}\\ \text{hydrochloride.}}}{C^{10}H^6N^2.HCl} + H^2O = \underset{\text{Naphthol.}}{C^{10}H^8O} + N^2 + HCl.$$

$$\underset{\text{Naphthol.}}{C^{10}H^8O} + \underset{\substack{\text{Nitric}\\ \text{acid.}}}{2NHO^3} = 2H^2O + \underset{\text{Dinitronaphthol.}}{C^{10}H^6(NO^2)^2O}$$

The dinitronaphthol separates in yellow needles which may be purified by recrystallisation from alcohol; or better in most cases by solution in ammonia, and repeated crystallisation of the resulting ammonium salt (Martius). See also Balló (*Zeitschr. f. Chem.* [2] vi. 51).

The same compound is obtained by adding a solution of α naphthyl-sulphuric acid (p. 860) to nitric acid; the liquid then turns red even in the cold, and deposits yellow crystalline dinitronaphthol, but the action is greatly facilitated by a gentle heat. The product is most easily purified by crystallisation from chloroform. β Napthyl-sulphuric acid treated in a similar manner does not yield any nitrated naphthol (Darmstädter a. Wichelhaus).

Dinitronaphthol forms sulphur-yellow crystals, which are especially lustrous and well defined when deposited from chloroform. It melts at 138° (Darmstädter a. Wichelhaus). It is nearly insoluble in boiling water, slightly soluble in alcohol, ether, and benzol; does not volatilise with vapour of water. It is dissolved without alteration by cold nitric acid, but by prolonged boiling therewith it is converted into oxalic and phthalic acids. It is an acid, decomposing carbonates with effervescence, and forming orange-red to minium-coloured salts, soluble in alcohol, and in some instances soluble in water. The *ammonium salt* separates on mixing a hot ammoniacal solution of the acid with concentrated solution of sal-ammoniac, as an orange-coloured precipitate which crystallises from boiling water in thin needles. The *calcium salt*, $[C^{10}H^5(NO^2)^2O]^2Ca + 6H^2O$, forms long orange-yellow needles somewhat sparingly soluble in water, and becoming red, with loss of water, at 120°. The *silver salt*, $C^{10}H^5(NO^2)OAg$, is a red flocculent precipitate, the solution of which in hot ammonia deposits crystals of the argent-ammonium salt. The *ethylic ether*, $C^{10}H^5(NO^2)^2O . C^2H^5$, formed by heating the silver salt with ethyl iodide to 100°, crystallises from alcohol in long yellow needles melting at 88°, insoluble in water (Martius).

Dinitronaphthol is one of the most beautiful and permanent of yellow dyes, colouring silk and wool, without the aid of a mordant, in all shades from light lemon to deep gold-yellow. It is isomeric with the yellow naphthalene dye (perhaps β dinitronaphthol) which was patented in this country in 1863 in the name of W. Newton (*London Journal of Arts*, 1863, December, p. 348). This latter, prepared by boiling 100 pts. naphthalene with 200 pts. nitric acid of sp. gr. 1·30, and designated by Martius as *dinitronaphthylic acid*, is much more soluble in alcohol than α dinitronaphthol, and is converted by reduction with tin and hydrochloric acid into a brown resinous mass, whereas α dinitronaphthol similarly treated yields the basic compound *diamidonaphthol*, $C^{10}H^6(NH^2)^2O$. The hydrochloric acid solution of this base supersaturated with potash, deposits, on exposure to the air, a yellow crystalline base, $C^{10}H^8N^2O$, which forms easily crystallisable, finely coloured, permanent salts, and is converted by boiling with water into an indifferent body, $C^{10}H^7NO^2$, crystallising in yellow-red needles:

$$C^{10}H^8N^2O + H^2O = C^{10}H^7NO^2 + NH^3.$$

This latter is converted by boiling with hydrochloric acid (according to the equation $C^{10}H^7NO^2 + H^2O = NH^3 + C^{10}H^6O^3$) into a compound which crystallises in yellow needles or laminæ very slightly soluble in water, more soluble in alcohol, very soluble in ether, subliming when heated, and yielding by oxidation oxalic and phthalic acids (Martius a. Griess, *Ann. Ch. Pharm.* cxxxiv. 375).

Oxynaphthol. $C^{10}H^8O^2 = C^{10}H^6(OH)^2$. *Naphthobioxyl.*—Produced by fusing disulphonaphthylene-sulphurous acid (v. 568), or its potassium salt, with potash:

$$C^{10}H^6(SO^3H)^2 + 2KOH = C^{10}H^6(OH)^2 + 2SO^3KH.$$

After precipitation from the potash solution by hydrochloric acid, and purification from a tarry substance by boiling with water, it crystallises in colourless needles or small rhombohedrons easily soluble in alcohol, ether, and chloroform, less easily in hot water. The solutions (not quite pure) exhibit a remarkable dichroïsm of blue and brown. Oxynaphthol dissolves easily in potash, the solution instantly turning black in contact with the air, and yielding with acids, after a while, a black precipitate. Heated in a test-tube to 230° it turns yellow and then brown, but does not fuse (Dusart, *Bull. Soc. Chim.* [2] viii. 200. Darmstädter a. Wichelhaus, *Deut. chem. Ges. Ber.* 1869, p. 113).

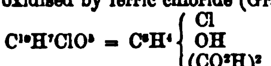
Dichloroxynaphthol, $C^{10}H^6Cl^2O^2 = C^{10}H^4Cl^2(OH)^2$, is formed by the action of reducing agents on dichloronaphthoquinone (p. 853):

$$C^{10}H^4Cl^2O^2 + H^2 = C^{10}H^4Cl^2(OH)^2.$$

The reduction is most easily effected by heating in the water-bath with aqueous hydriodic acid and a small quantity of phosphorus, till the yellow crystals of dichloronaphthoquinone become colourless. By washing these crystals with water, dissolving them in alcohol, and evaporating or precipitating with water, dichloroxynaphthol is obtained in colourless crystals which quickly turn reddish on exposure to the air. It is quite insoluble in cold water, only slightly soluble in hot water, easily in alcohol and ether. It melts at 135°–140°, turns brown and decomposes partially at a higher temperature. Alkalis dissolves it readily, forming a solution which is colourless at first, but soon acquires the colour of the chloroxynaphthalates. Ferric chloride reconverts it into dichloronaphthoquinone (Graebe, *Ann. Ch. Pharm.* cxlix. 5).

Dichlorodiacetoxynaphthol, $C^{10}H^4Cl^2(OC^2H^3O)^2$, is formed by heating dichloroxynaphthol with acetyl chloride. After washing and recrystallisation from alcohol, it forms long, colourless, silky needles melting at 236° and subliming in long prisms. It is insoluble in water, dissolves slightly in cold alcohol, easily in hot alcohol and ether. It is not attacked by potash, or oxidised by ferric chloride (Graebe, *loc. cit.*).

Chloro-dioxynaphthalic Acid.



$C^{10}H^7ClO^6 = C^8H^4\left\{\begin{matrix} Cl \\ OH \\ (CO^2H)^2 \end{matrix}\right.$

(Th. Hermann, *Ann. Ch. Pharm.* cli. 63; *Zeitschr. f. Chem.* [2] iv. 551; *Jahresb.* 1868, p. 382).—This acid is obtained, together with other products, by adding potassium chlorate in small portions to a mixture of moderately strong sulphuric acid and naphthalene, whereby chlorous acid is evolved, which then acts upon the naphthalene in the manner shown by the equation:

$$C^{10}H^8 + 3ClHO^2 = 2HCl + H^2O + C^{10}H^7ClO^5.$$

The product of the reaction consists of a liquid and a yellowish-red buttery mass. The liquid is decanted; the buttery mass repeatedly exhausted with warm water, as long as acid extracts are obtained; the acid liquid is repeatedly exhausted with ether; the ether evaporated; the residue is digested with benzol; the residue left after evaporation of the benzol is exhausted with warm water; and the solution is decolorised with animal charcoal. This solution when left to evaporate deposits the chlorinated acid in oily drops; these are dissolved in benzol, and the solution is left to evaporate in an open vessel. The syrupy liquid thus obtained gradually deposits crystals of phthalic acid, which may be removed by precipitating the very dilute solution with basic lead acetate; and the remaining liquid, freed from lead and again left to evaporate, yields the chlorinated acid. This, when dried over sulphuric acid, is an amorphous slightly coloured substance, moderately soluble in water, easily soluble in alcohol, ether, and benzol. When boiled with water, it very readily exchanges its chlorine for hydroxyl, so that it is not easily prepared in any considerable quantity.

Dioxynaphthalic Acid. $C^{10}H^8O^6 = C^8H^4\left\{\begin{matrix}(OH)^2\\(COOH)^2\end{matrix}\right.$ (Hermann, *loc. cit.*).—Produced by boiling the chlorinated acid with water, or more readily with baryta-water. It is most easily purified by converting it several times into the acid barium salt. When first separated from this salt, it forms a viscid substance, which however, when left at rest for some time, or more quickly if rubbed with a glass rod, begins to crystallise, and solidifies in a few days to a radio-crystalline mass. According to Carius, the crystals are moderately oblique monoclinic prisms, tabular from predominance of the face $\infty P\infty$. The acid is extremely soluble in water, alcohol, and ether; insoluble in benzol. The solution has a strong acid reaction, decomposes carbonates, and reduces silver from the ammoniacal solution of the nitrate at the boiling heat. Nitric acid oxidises it to phthalic acid. When heated it softens below 100°, melts at 126°, and does not resolidify till cooled to a much lower temperature. Heated between watch-glasses, it yields a sublimate of a sparingly soluble acid and a brown residue which at a higher temperature gives off yellow strong-smelling vapours, condensing partly in the crystalline form, partly in oily drops. Heated to 180° with hydriodic acid of 50 p. c., it yields, with separation of iodine, but without evolution of carbon dioxide, a somewhat sparingly soluble acid, which crystallises in rhombic prisms, sublimes like benzoic acid, forms a yellow precipitate with ferric chloride, and in neutral solution, white precipitates with lead and silver salts.

Dioxynaphthalic acid is bibasic. Most of its salts are easily soluble in hot water. The acid salts crystallise more readily than the neutral salts. Lead acetate produces in the cold solution of the neutral barium salt a precipitate easily soluble in acetic acid; ferric chloride forms a yellow-brown precipitate even in the acid solution. The following dioxynaphthalates have been examined:

$C^{10}H^6O^6K^2$,	very deliquescent, microscopic, rhombic prisms.
$C^{10}H^7O^6K + H^2O$,	spherical groups of needles, or rhombic prisms or pyramids.
$C^{10}H^7O^6(NH^4)$,	slender needles.
$C^{10}H^6O^6Ba + 3H^2O$,	rhombic prisms; anhydrous at 110°.
$(C^{10}H^7O^6)^2Ba$,	monoclinic prisms, or nodular groups of needles.
$(C^{10}H^6O^6)^2Ca(NH^4)^2 + 2H^2O$,	many-sided monoclinic prisms; anhydrous at 120°; decomposing at 140°.
$(C^{10}H^6O^6)^2Ca(NH^4)^2$,	shining monoclinic prisms.
$(C^{10}H^6O^6)^2Cu(NH^4)^2$,	blue rhombic prisms.
$(C^{10}H^6O^6)^4Cu^3H^2 + 2H^2O$,	microscopic monoclinic prisms, obtained by double decomposition of the acid barium salt.
$C^{10}H^6O^6Pb$,	white amorphous precipitate.
$4C^{10}H^6O^6Pb.PbH^2O^2 + 4H^2O$,	monoclinic tables, obtained by boiling the neutral salt with excess of lead acetate.

The solution of this last salt in hot water containing a few drops of nitric acid deposits on cooling, monoclinic prisms of the salt $(C^{10}H^6O^6)^{12}Pb^7H^{10} + 16H^2O$.

Dioxynaphthalic chloride, $C^{10}H^6O^4Cl^2$ or $C^8H^4\left\{\begin{matrix}Cl^2\\(COOH)^2\end{matrix}\right.$, is formed by the action of phosphorus pentachloride on potassium dioxynaphthalate. It is an oily liquid decomposed by water with reproduction of the acid, and by alcohol with formation of diethylic dioxynaphthalate, $C^{10}H^{6}O^{6}.(C^{2}H^{5})^{2}$.

NAPHTHYL CYANIDE. $C^{10}H^{7}CN$.—Syn. with MONOCYANONAPHTHALENE (p. 847).

NAPHTHYL ETHERS. Naphthyl Acetates or **Acetyl-naphthols,** $C^{10}H^{7}(C^{2}H^{3}O)O$, are obtained by treating naphthol with acetyl chloride in a retort with upright condenser ultimately at a gentle heat, distilling off the excess of acetyl chloride, dissolving the residue in alcohol, and evaporating. α *Acetyl-naphthol* washed with water and dried in a vacuum over caustic potash forms a clear, yellowish, oily, nearly inodorous liquid, insoluble in water, easily soluble in alcohol, ether, and chloroform. When it is distilled with aqueous vapour, or even when its alcoholic solution is evaporated over the water-bath, it is resolved into naphthol and acetic acid. β *Acetyl-naphthol* crystallises from its alcoholic solution by evaporation at a gentle heat. When purified by repeated crystallisation from alcohol, and dried in a vacuum over caustic potash, it forms small, soft, shining, needle-shaped crystals having a faint but agreeable odour of anise, easily soluble in alcohol, ether, and chloroform, but insoluble in water. Melts at 60°. Decomposed by heat, like the α ether (Schäffer).

Naphthyl Benzoates or **Benzoyl-naphthols,** $C^{10}H^{7}(C^{7}H^{5}O)O$, are obtained by heating naphthol with benzoyl chloride. The α compound separates from solution in ether by evaporation as a yellowish oil which solidifies after a few days to a crystalline mass, and when recrystallised from ether-alcohol forms large shining tables and prisms melting at 56°. It dissolves in boiling alcohol, and separates on cooling as an oil which soon solidifies to a crystalline mass. By heating with sulphuric acid it is resolved into benzoic and naphthyl-sulphurous acids. β *Benzoyl-naphthol* is sparingly soluble in ether, easily in boiling alcohol, and crystallises therefrom on cooling in nodular groups of slender needles melting at 107°. By heating with alcoholic potash it is resolved into benzoic acid and β naphthol (Maikopar).

Naphthyl Ethylates or **Ethyl-naphthols,** $C^{10}H^{7}(C^{2}H^{5})O$, are produced by heating naphthol with an equivalent quantity of potassium hydrate and excess of ethyl iodide in alcoholic solution, in a retort with upright condenser. On separating the potassium iodide thereby formed, and expelling the alcohol, ethyl-naphthol remains, and may be distilled over with vapour of water.

α Ethyl-naphthol is a yellowish oily liquid which has a peculiar odour, sinks in water, boils at 272° (corr. 280·7°), and does not solidify at −5°. β Ethyl-naphthol is at ordinary temperatures a nearly colourless crystalline mass having an agreeable odour like that of pine-apples. It melts at 33°; dissolves easily in alcohol, ether, chloroform, and benzol, but is insoluble in water (Schäffer).

Naphthyl Phosphate, $PO^{4}(C^{10}H^{7})^{3} = PO(C^{10}H^{7}O)^{3} = \left.\begin{matrix}(PO)''' \\ (C^{10}H^{7})^{3}\end{matrix}\right\}O^{3}$ (Schäffer, *Ann. Ch. Pharm.* clii. 289).—Produced by gently heating naphthol with an equivalent quantity of phosphorus pentachloride, and purified by solution in alcohol, decoloration with animal charcoal, and repeated crystallisation. The formation of the phosphate is probably preceded by that of the monochloride; thus:

$$C^{10}H^{7}OH + PCl^{5} = C^{10}H^{7}Cl + HCl + POCl^{3}$$

and

$$3C^{10}H^{7}OH + POCl^{3} = PO(C^{10}H^{7}O)^{3} + 3HCl.$$

α Naphthyl phosphate forms small colourless crystals, easily soluble in ether and chloroform, sparingly soluble in alcohol, insoluble in water. Melting point 145°.

β Naphthyl phosphate crystallises in small white inodorous needles, easily soluble in ether and chloroform, sparingly in cold, easily in hot alcohol; insoluble in water. Melting point 108° nearly.

Naphthyl-sulphuric Acids. $C^{10}H^{8}SO^{4} = C^{10}H^{6}\left\{\begin{matrix}OH \\ SO^{3}H\end{matrix}\right. = \left.\begin{matrix}C^{10}H^{7} \\ (SO^{2})'' \\ H\end{matrix}\right\}O^{2}$ (Schäffer, *Ann. Ch. Pharm.* clii. 293).—Produced by heating naphthol with strong sulphuric acid in the water-bath till it is completely dissolved and is no longer precipitated by water, then diluting with water, boiling, and neutralising with lead carbonate. The resulting lead salt, purified by recrystallisation and decomposed by hydrogen sulphide, yields a solution of the acid which may be crystallised by evaporation over the water-bath, and finally in a vacuum over sulphuric acid.

α *Naphthylsulphuric acid* forms long white radiating needles, unctuous to the touch, very deliquescent, easily soluble in water and in alcohol; melting, with brown coloration, at 101°. It dissolves easily in nitric acid, the solution after some time depositing crystalline dinitronaphthol. Its solution mixed with ferric chloride assumes a deep blue colour, changing to green when heated and becoming blue again on cooling. It is not coloured by chloride of lime. The *calcium salt*, $(C^{10}H^7SO^4)^2Ca + 3H^2O$, forms small colourless shining laminæ easily soluble in water, less soluble in alcohol, decomposing at 100°. *Lead salts.*—A solution of the acid neutralised with lead carbonate yields two lead naphthyl-sulphates, one containing $C^{10}H^6SO^4Pb$, crystallising in microscopic needles sparingly soluble in water, almost insoluble in alcohol, easily soluble in acidulated water; the other, $(C^{10}H^7SO^4)^2Pb$, crystallising in nodular groups of needles, easily soluble in water, somewhat less soluble in alcohol.

β *Naphthyl-sulphuric acid* forms small laminar crystals unctuous to the touch, melting at 125°, not deliquescent. With nitric acid it forms in the cold a deep red solution with a tinge of blue; the colour disappears at the boiling heat, but without formation of a separable nitro-compound. The aqueous solution of the β acid mixed with ferric chloride assumes a faint green colour in the cold, and deposits brown flocks when heated. With chloride of lime it assumes a yellow colour, becoming somewhat deeper on addition of ammonia. The *calcium salt*, $(C^{10}H^7SO^4)^2Ca + 5H^2O$, forms very light silky laminæ easily soluble in water and alcohol, giving off their water in a vacuum over sulphuric acid, decomposing at 100°. There is but one *lead salt* of β naphthyl-sulphuric acid, viz. $(C^{10}H^7SO^4)^2Pb + 6H^2O$, which forms small silvery very light crystalline laminæ easily soluble in water, somewhat less soluble in alcohol.

Naphthylsulphurous Acid. $C^{10}H^8SO^3 = C^{10}H^7.SO^3H$.—*Naphthalene-sulphuric Acid. Sulphonaphthalic Acid.*—Faraday obtained this acid in two modifications, distinguished from another by the behaviour of their barium salts when heated, the one burning with flame, the other merely smouldering (v. 560). Merz (*Zeitschr. f. Chem.* [2] iv. 393), who distinguishes the former as α, the latter as β naphthylsulphurous acid, finds that these two acids may be most easily separated by means of their lead salts, the α lead salt being much more soluble in water and in alcohol than the β salt. All the α salts are in fact more soluble than the corresponding β salts. *Potassium salts*, $2C^{10}H^7SO^3K + H^2O$.—The α salt crystallises from alcohol in laminæ, the β salt in needles. The α salt dissolves in 13 pts. water and in 108 pts. alcohol at 11°; the β salt in 15 pts. water and 115 pts. alcohol at 10°. *Barium salts*, $(C^{10}H^7SO^3)^2Ba + H^2O$.—The α salt dissolves in 87 pts. water and in 350 pts. alcohol at 10°; the β salt in 290 pts. water and in 1950 pts. alcohol at 10°. *Calcium salts.*—Crystallise in laminæ; the α salt, $(C^{10}H^7SO^3)^2Ca + 2H^2O$, dissolves in 16·5 pts. water and 19·5 pts. alcohol at 10°. The β salt forms anhydrous crystals soluble in 76 pts. water and in 137 pts. alcohol at 10°. *Lead-salts.*—The α salt crystallises from water or alcohol in shining laminæ soluble in 27 pts. water and in 11 pts. alcohol at 10°. The β salt forms scales or crusts containing $\frac{2}{3}$ mol. water or anhydrous, soluble in 115 pts. water and in 305 pts. alcohol at 10°.

α Naphthylsulphurous acid, separated from the lead salt by hydrogen sulphide, is completely resolved, by heating to 200° with hydrochloric acid, into sulphuric acid and naphthalene: $C^{10}H^7SO^3H + H^2O = SO^4H^2 + C^{10}H^8$. The β acid similarly treated remains for the most part undecomposed (Merz).

The potassium salts of the two acids heated with potassium cyanide yield α and β naphthyl cyanide (p. 847).

The following observations apply to the α acid and its derivatives:

Naphthylsulphurous chloride, $C^{10}H^7SO^2Cl$, prepared by the action of phosphorus pentachloride on sodium naphthyl-sulphite, is decomposed in alcoholic solution by sodium-amalgam, in such a manner as to yield naphthalene and sulphurous acid:

$$C^{10}H^7SO^2Cl + H^2 + H^2O = HCl + C^{10}H^8 + H^2SO^2;$$

whereas in acid solution (with zinc and sulphuric acid) it yields naphthyl sulphydrate:

$$C^{10}H^7SO^2Cl + H^6 = C^{10}H^7HS + HCl + 2H^2O.$$

When sodium-amalgam acts upon the chloride dissolved in pure ether, *naphthylsulphurous hydride*, $C^{10}H^8SO^2 = C^{10}H^7SO^2H$, is produced as a thickish oil, slightly soluble in water, easily in alcohol or ether, converted by oxidation in the air into naphthylsulphurous acid, and by treatment with zinc and sulphuric acid into naphthyl sulphydrate (Otto a. Mories, *Ann. Ch. Pharm.* cxlvii. 164; *Jahresb.* 1867, p. 718).

Bromonaphthylsulphurous Acid. $C^{10}H^6BrSO^3H$.—Of this acid there are three modifications, the first of which is formed by dissolving monobromonaphthalene in

1,000 pts. of cold alcohol of 94 p. c.; soluble in 38 pts. of boiling and about 52 pts. of cold ether; in 28 pts. boiling and about 500 pts. cold glacial acetic acid; in 2 pts. hot and 1 pt. cold benzol. From solution in alcohol or acetic acid, it crystallises in feathery or laminated groups of flat needles; melts somewhat above 175° to a colourless liquid; and solidifies again in the crystalline form only when the temperature has not been raised above a certain point. At 220° it boils and may be distilled undecomposed in quantities not exceeding 10 grams. It is not decomposed by alcoholic potash-solution or even by fusion with potassium hydrate. Nitric acid of sp. gr. 1·3 converts it into oxylepidene. When gently heated with phosphorus pentachloride, it forms a reddish liquid, which solidifies when washed with water, dissolves easily in alcohol and ether, and crystallises therefrom in needles (Zinin).

Dibromolepidene, $C^{28}H^{18}Br^2O$, is formed on adding bromine in slight excess to a solution of lepidene in acetic acid, and separates in needle-shaped crystals insoluble in water, soluble in 410 pts. of hot alcohol, 66 pts. of boiling acetic acid, and 50 pts. of boiling ether, and crystallises therefrom in thin tables or laminæ. It melts at 190°, and solidifies in the crystalline or amorphous state, according to the temperature to which it has been raised. With nitric acid it forms a needle-shaped body which reacts similarly to oxylepidene.

Oxylepidene, $C^{28}H^{20}O^2$, is most readily prepared by heating lepidene to the boiling point with 10 pts. of glacial acetic acid, and adding a mixture of 1 pt. nitric acid of sp. gr. 1·5 and 3 pts. glacial acetic acid, the oxylepidene then crystallising out on cooling. It forms yellow needles (4-sided prisms) insoluble in water, nearly insoluble in ether and cold alcohol, soluble in 200 pts. of boiling alcohol of 94 p. c., in 22 pts. of hot acetic acid, and easily in benzene. It melts at 220° and resolidifies in the crystalline form on cooling; but after being heated to its boiling point, it forms on cooling a yellow resinous substance, easily soluble in alcohol and ether, and separating therefrom with different properties. Oxylepidene dissolved in hot acetic acid is completely reduced by zinc to lepidene; by boiling with alcoholic potash-solution it is converted into a crystalline body, separable by water and differing in its properties from oxylepidene (Zinin).

Lepidene and oxylepidene are analogous in composition to thionessal and tolallyl sulphide; thus:

Lepidene,	$C^{28}H^{20}O$	Oxylepidene,	$C^{28}H^{20}O^2$
Thionessal,	$C^{28}H^{20}S$	Tolallyl sulphide,	$C^{28}H^{20}S^2$,

and may be formed from thionessal and tolallyl sulphide respectively by treatment with hydrochloric acid and potassium chlorate (Limpricht).

Oxylepidene is converted by the most various reducing agents into lepidene, but the latter cannot be deprived of any further portion of oxygen, even by passing it over heated zinc-powder. Oxylepidene heated with phosphorus pentachloride yields the same products as lepidene, namely, chlorinated derivatives of the latter. The following compounds have been obtained by Dorn:

Dichloroxylepidene, $C^{28}H^{18}Cl^2O^2$, is prepared by treating dichlorothionessal with hydrochloric acid and potassium chlorate. It forms white needles melting at 178°, and is converted by reducing agents into dichlorolepidene, $C^{28}H^{18}Cl^2O$, which forms white needles melting at 156°.

Oxylepidene heated in sealed tubes with phosphorus pentachloride, or (to diminish the pressure) with phosphorus oxychloride, yielded:

1. *Pentachlorolepidene*, $C^{28}H^{15}Cl^5O$, in white crystals melting at 186°, very slightly soluble in alcohol and ether.—2. *Hexchlorolepidene*, $C^{28}H^{14}Cl^6O$, a yellow amorphous substance, melting at 80°–90°, easily soluble in alcohol and ether.—3. *Octochlorolepidene*, $C^{28}H^{12}Cl^8O$, an orange-yellow amorphous substance, softening at 70°, melting at 97°, easily soluble in alcohol and ether.

LEPIDOMELANE. This variety of mica, hitherto found only at one locality in Sweden (iii. 574), occurs, together with danalite, another variety of mica called *cryophyllite*, and a zircon-like mineral, in the granite of Rockport, Massachusetts. The lepidomelane occurs in black six-sided prisms with dark green streak, hardness about 3, and sp. gr. 3·169. Analysis gave:

SiO^2	SiF^4	Al^2O^3	Mn^2O^3	Fe^2O^3	FeO	MgO	K^2O	Li^2O	H^2O	
39·55	0·62	16·73	0·60	12·07	17·48	0·62	10·66	0·59	1·50	= 100·42,

agreeing with the general formula $(M^4; M^2)SiO^4$ (J. P. Cooke, jun., *Sill. Am. J.* [2] xliii. 217).

LEUCANILINE. On the methylated derivatives of this base, produced by the decomposition of iodine-green, see ANILINE (p. 764).

solution into a cylindrical vessel filled with alcohol, a liquid is formed, perfectly transparent, with light rose-colour by transmitted light, but exhibiting in reflected light a strong and peculiar fluorescence, giving an appearance of opacity, as if a precipitate were being formed, and diffusing itself through the liquid in clouds of a fiery-red colour.

Naphthylamine-red is also formed by treating azodinaphthyl-diamine with naphthylamine, ammonia being evolved at the same time. In this case its formation from naphthylamine may be represented by the two following equations:

$$\underset{\text{Naphthyl-amine.}}{2C^{10}H^9N} + HNO^2 = 2H^2O + \underset{\text{Azodinaphthylamine.}}{C^{20}H^{15}N^3}$$

$$\underset{\text{Azodinaphthyldiamine.}}{C^{20}H^{15}N^3} + C^{10}H^9N = NH^3 + \underset{\text{Naphthylamine-red.}}{C^{30}H^{21}N^3}$$

Naphthylamine-red forms splendidly crystallised colouring matters with the iodides of methyl and ethyl (Hofmann, *Deut. chem. Ges. Ber.* 1869, pp. 375, 412; *Zeitschr. f. Chem.* [2] v. 632, 694).

On the action of acids on naphthylamine, see Chapman (*Chem. Soc. J.* [2] iv. 135, 329).

NAPHTHYL-CARBOXYLIC ACID. Syn. with NAPHTHOIC ACID (p. 851).

NAPHTHYL-DIAMINE, $\left.\begin{matrix}(C^{10}H^7)''' \\ H^3\end{matrix}\right\}N^2$, and **NAPHTHYLENE-DIAMINE,** $\left.\begin{matrix}(C^{10}H^6)'' \\ H^4\end{matrix}\right\}N^2$.—Naphthyl-diamine is produced, together with naphthylamine and pyridine (as secondary product), by the action of nascent hydrogen on azodinaphthyldiamine:

$$\left.\begin{matrix}(C^{10}H^7)^2 \\ N''' \\ H\end{matrix}\right\}N^2 + H^4 = \left.\begin{matrix}C^{10}H^7 \\ H^2\end{matrix}\right\}N + \left.\begin{matrix}(C^{10}H^7)''' \\ H^3\end{matrix}\right\}N^2.$$

When a saturated alcoholic solution of azodinaphthyldiamine is digested with tin and strong hydrochloric acid, the decanted yellow solution evaporated, the aqueous extract of the residue freed from tin by hydrogen sulphide, and the filtrate evaporated as much as possible without contact of air, a residue is left, which, after recrystallisation from a small quantity of water, with addition of strong hydrochloric acid, and washing with dilute hydrochloric acid, consists of the hydrochlorides of naphthylamine and naphthyl-diamine; the pyridine salt remains in the mother-liquor. The separation of the two salts is most easily effected by repeated digestion with absolute alcohol, which dissolves chiefly the hydrochloride of naphthylamine, while the naphthyl-diamine salt remains undissolved.

Naphthyl-diamine precipitated from the hydrochloride by ammonia forms splendid shining scales, which on exposure to the air are very quickly converted into a dark green mass. By distillation in a stream of hydrogen it is obtained as a pale yellow oil of very high boiling point, solidifying to a crystalline mass on cooling. It is easily soluble in alcohol, ether, and benzol. The *hydrochloride*, $C^{10}H^{10}N^2.2HCl$, crystallises from hot water in laminæ, and is almost completely precipitated from its aqueous solution by hydrochloric acid. The gold and platinum salts form dingy green needles. The *sulphate*, $C^{10}H^{10}N^2.H^2SO^4$, is precipitated by dilute sulphuric acid from the hot-saturated solution of the hydrochloride in long needles, or as a light brown crystalline powder nearly insoluble in cold water and in alcohol. The *nitrate* is a nodular crystalline mass; the *oxalate* crystallises in tufts.

The alcoholic solution of naphthyl-diamine forms with silver nitrate a white precipitate, which quickly decomposes with separation of metallic silver; the precipitate formed with mercuric chloride likewise decomposes in drying. On mixing the alcoholic solution of the base with carbon bisulphide, hydrogen sulphide is gradually evolved, and dark garnet-red crystals separate, sparingly soluble in alcohol, ether, and benzol. Potassium nitrite, ferric chloride, potassium dichromate or ferricyanide, produce, in dilute solutions of naphthyl-diamine salts a splendid green colour; in more concentrated solutions a green flocculent precipitate; this reaction is very delicate and serves to distinguish naphthyl-diamine from naphthylene-diamine (*infra*), which is coloured brown-red or chestnut-brown by the oxidising agents above mentioned. The green substance is coloured violet by ammonia and brown-red by hydrochloric acid; by distillation, either alone or with potash, it reproduces naphthylamine (Perkin, *Chem. Soc. J.* [2] iii. 173).

Naphthylene-diamine hydrochloride, $C^{10}H^6(NH^2)^2.2HCl$, is formed by boiling dinitro-naphthalene with tin and hydrochloric acid, and crystallises from the series, the specific refractive energy increases as the series advances, but that the amount of its variation is less between the higher than between the lower terms of the series.

Landolt (*Pogg. Ann.* cxxii. 545; cxxiii. 595; *Jahresb.* 1864, p. 101) simplifies the expression of these relations, especially of the last, by adopting, instead of the specific refractive energy, the product of this fraction by the molecular weight of the compound, $P.\frac{\mu-1}{d}$; this is called the refraction-equivalent. In homologous series the refraction increases in all cases for a difference of CH^2, by a nearly equal amount, the mean increment in the fatty acids, alcohols, &c., being 7·60. The first and third of the above laws remain true for refraction-equivalents to the same extent as for specific refractive energies. The expression of the second becomes: *The refraction-equivalent of a mixture or compound is the sum of the refraction-equivalents of its components.*

This last law gives the means of determining the refraction-equivalents of elements from those of their compounds. Landolt has shown, by comparison of the optical properties of a large number of organic compounds, that the refraction-equivalent is increased by addition of either carbon, hydrogen, or oxygen, but by somewhat different amounts according to the type to which the compound belongs, these values varying for C from 4·75 to 5·43, for H from 1·06 to 1·33, for O from 2·45 to 3·24. The mean refraction-equivalents of these three elements in the homologous fatty alcohols and acids are:

C	H	O*
5·00	1·30	3·00

By means of these values, the refraction-equivalent R of a compound of carbon, hydrogen, and oxygen may be calculated according to the formula,

$$R = mr + m'r' + m''r'',$$

where m, m', m'' denote the numbers of the atoms of the three elements, and r, r', r'' their refraction-equivalent: thus in the case of ethyl oxide, $C^4H^{10}O$:

$$4 \times 5·0 + 10 \times 1·3 + 3·0 = 36·0$$

Refraction-equivalent deduced from observation . . . = 36·26.

The values above given for the refraction-equivalents of C, H, and O agree very nearly with those deduced from the experiments of Gladstone and Dale already cited. Gladstone has subsequently determined, by similar methods, the refraction-equivalents of chlorine, bromine, tin, iodine, and mercury; and Haagen (*Pogg. Ann.* cxxxi. 117), by examining a variety of liquid haloïd compounds, has deduced for several of these elements, refraction-equivalents agreeing with those found by Gladstone, together with those of arsenic, antimony, and silicon.

The fact, previously established by Gladstone and Dale, that a substance when dissolved retains the same specific refractive energy, and consequently the same refraction-equivalent, as in the solid state, affords the means of determining the refraction-equivalents of a great number of solid bodies which could not otherwise be ascertained. By determining the refractive indices of a series of chlorides, bromides, and iodides dissolved in water, Gladstone has shown that a chloride has, in each case, a refraction-equivalent about 6 less than the corresponding bromide, and about 17 less than the corresponding iodide; and that a potassium salt has, in each case, a refraction-equivalent about 3·2 greater than that of the corresponding sodium salt, about 4 greater than the lithium salt, and about 3·5 less than the ammonium salt. Hence it seems to follow: 1. That the different salts are really comparable with one another in this respect.—2. That each halogen and each metal retains its own refractive power, with whatever other elements it is combined.—3. That if the value of any one of these elements can be ascertained with certainty, all the rest may also be determined.

Experiments conducted on these principles have been extended by Gladstone to about 180 different salts, containing 28 inorganic salt-radicles and 33 metals. The results are tabulated in a paper recently communicated to the Royal Society (*Phil. Trans.* 1870, p. 9; abstr. *Proc. Roy. Soc.* 1868, p. 439).

The refraction-equivalents of the elementary bodies deduced from these results are given in the following table:

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* These values differ but slightly from those of the free elements deduced by Landolt from the observations of Schrarf, Dulong, and Regnault, viz. C = 4·85, H = 1·54, O = 3·04.

Hydrochloride of dimethyl-nornarcotine treated with *ferric* or ***platinic chloride***, forms methyl-noropianic acid and cotarnine; thus:

$$C^{19}H^{15}(CH^3)^2NO^7 + O = C^8H^5(CH^3)O^5 + C^{11}H^{10}(CH^3)NO^3.$$

Methyl-nornarcotine heated with water yields in like manner normeconin and cotarnine:

$$C^{19}H^{16}(CH^3)NO^7 = C^8H^6O^4 + C^{11}H^{10}(CH^3)NO^3;$$

with oxidising agents, noropianic acid and cotarnine:

$$C^{19}H^{16}(CH^3)NO^7 + O = C^8H^6O^5 + C^{11}H^{10}(CH^3)NO^3;$$

and nornarcotine yields with heated water and with oxidising agents, normeconin or noropianic acid respectively, and cotarnimide:

$$\underset{\text{Nornarcotine.}}{C^{19}H^{17}NO^7} = \underset{\text{Normeconin.}}{C^8H^6O^4} + \underset{\text{Cotarnimide.}}{C^{11}H^{11}NO^3}$$

$$\underset{\text{Nornarcotine.}}{C^{19}H^{17}NO^7} + O = \underset{\text{Noropianic acid.}}{C^8H^6O^5} + \underset{\text{Cotarnimide.}}{C^{11}H^{11}NO^3}$$

The following table exhibits a comparative view of the physical properties and reactions of nornarcotine and its methylated derivatives, and of cotarnine:

Characters of Narcotine, &c.

	Trimethyl-nornarcotine (ordinary narcotine), $C^{22}H^{23}NO^7$	Dimethyl-nornarcotine, $C^{20}H^{21}NO^7$	Methyl-nornarcotine, $C^{20}H^{19}NO^7$	Nornarcotine, $C^{19}H^{17}NO^7$.	Cotarnine, $C^{12}H^{13}NO^3$
Form . .	White crystals	White or amorphous	White, when freshly ppd., sometimes brown; amorphous	White, turning brown immediately on exposure to air; amorphous.	*White*; generally buff-coloured: *crystalline*
Solubility in:					
Water . .	Almost insol.	Almost insol.	Almost insol.	Almost insol.	Almost insol.
Alcohol .	Soluble	Very soluble	Insoluble	Insoluble	Very soluble
Ether . .	Soluble	Slightly sol.	Insoluble	Insoluble	Very soluble
Concentrated solution of Chloride. .	Not ppd. by HCl. Solution in HCl not ppd. by water	Ppd. partially by HCl. Solution in strong HCl ppd. by water: the ppd. chloride is tarry	Mostly ppd. by HCl. Solution in strong HCl ppd. by water; ppd. chloride granular	Almost wholly ppd. by HCl. Solution in strong HCl ppd. by water; ppd. chloride granular	Not ppd. by HCl. Solution in HCl not ppd. by water
Taste of Chloride .	Bitter	Bitter	Astringent	Tasteless	Bitter
Reactions of the chlorides in solution with: $PtCl^4$*	Yellow pp.	Yellow pp.	Yellow pp., slowly turning brown	Yellow pp., immediately turning brown	Yellow pp.
KHO	Pp. insoluble in excess	Pp. soluble in excess	Pp. slightly sol. in excess	Pp. soluble in excess	Pp. slightly sol. in excess
NH^4HO	Pp. insoluble in excess	Pp. slightly sol. in excess	Pp. soluble in excess	Pp. soluble in excess	Pp. soluble in excess
Na^2CO^3	Pp. insoluble in excess	Pp. insoluble in excess	Pp. soluble in excess	Pp. soluble in excess	Pp. soluble in excess

* All these precipitates decompose on boiling with excess of platinum chloride.

According to Gobley (*J. Pharm.* [4] ii. 156), narcotine may be extracted from opium—together with a fatty oil and a substance resembling caoutchouc—by digestion with oil of turpentine at 100°.

Narcotine Tri-iodide, $C^{22}H^{23}NO^7HI^3$, is formed by mixing an alcoholic solution of narcotine with hydrochloric acid, adding the calculated quantity of iodine, and then water till a permanent turbidity is produced. On stirring the liquid, the tri-iodide separates in shining laminæ, and an additional quantity may be obtained by adding more water. This compound is moderately soluble in alcohol, but undergoes a remarkable alteration when boiled therewith, the solution on cooling depositing the tri-iodide of a new base, tarconine, $C^{12}H^{11}NO^3$, containing 2 at. hydrogen less than cotarnine:

$$\underset{\substack{\text{Narcotine}\\ \text{tri-iodide.}}}{3(C^{22}H^{23}NO^7.HI^3)} + H^2O = \underset{\substack{\text{Tarconine}\\ \text{tri-iodide.}}}{C^{12}H^{11}NO^3.HI^3} + \underset{\substack{\text{Opianic}\\ \text{acid.}}}{C^{10}H^{10}O^5} + 4HI +$$

$$\underset{\substack{\text{Narcotine}\\ \text{Hydriodide.}}}{2(C^{22}H^{23}NO^7.HI)}$$

(Jörgensen, *Deut. chem. Ges. Ber.* 1869, 460; *Zeitschr. f. Chem.* [2] v. 673).

NEPHRITE. For analyses of this mineral from the pile-buildings of the Swiss lakes and other localities, see Fellenberg (*Jahresb.* 1865, p. 880); Damour (*Compt. rend.* lxi. 313, 357; *Jahresb.* 1865, p. 880).

NEPHROZYMASE. This name is applied by Béchamp (*Bull. Soc. Chim.* [2] iii. 213) to a soluble ferment existing in the urine of man, the dog, and the rabbit, and capable of converting starch into sugar.

NEURINE. Syn. with CHOLINE (p. 448).

NICKEL. The atomic weight of this metal has been redetermined by Russell (*Chem. Soc. J.* [2] vii. 294) by measuring the volume of hydrogen evolved on dissolving a known weight of the pure metal in hydrochloric acid. (See ANALYSIS OF GASES, p. 142.) The mean of four closely agreeing experiments gave for the atomic weight of nickel the number 58·70, which is very nearly the same as that which Russell formerly obtained (iv. 40) by reducing the pure monoxide with hydrogen, viz. 58·74.

Different but less trustworthy results have been obtained by Sommaruga (*Jahresb.* 1866, p. 244) and by Winkler (*ibid.* 1867, p. 289). The former, by analysis of niccolo-potassic sulphate, $(SO^4)^2NiK^2 + 6H^2O$, obtained the number 58; the latter, by reducing a neutral solution of sodio-auric chloride with metallic nickel, and weighing the gold precipitated, found Ni = 59·06.

Detection of Nickel.—A solution of a nickel salt mixed with sodium acetate and *hypochlorite*, and heated to the boiling point, deposits a deep blue, nearly black peroxide forming a specular coating on the glass; the reaction is extremely delicate, and every trace of nickel is thereby removed from the liquid (Popp, *Ann. Ch. Pharm.* cxxxi. 363; see also Wicke, *Zeitschr. f. Chem.* [2] i. 86; *Jahresb.* 1865, p. 267). *Sodium hyposulphite* added to nickel salts at the boiling heat throws down black nickel sulphide, probably also forming trithionate and chloride of sodium:

$$NiCl^2 + 2Na^2S^2O^3 = NiS + Na^2S^3O^6 + 2NaCl.$$

The precipitate is not attacked by strong sulphuric or boiling hydrochloric acid, but is oxidised by nitric acid to nickel sulphate (W. Gibbs, *Sill. Am. J.* [2] xxxvii. 346).

Potassium sulphocarbonate colours a nickel solution crimson-brown, or, if very dilute, rose-red. The solution to be tested is first freed from cobalt by potassium nitrite, and the filtrate is made alkaline with ammonia, mixed with sal-ammoniac, and precipitated with a little colourless ammonium sulphide. The filtrate from this precipitate yields, when strongly concentrated by evaporation, a precipitate of nickel sulphide. This precipitate is washed on a filter, dried, ignited, treated with a little nitric acid, and evaporated. The saline residue is dissolved in water and added to about 50 c. c. water containing 1 or 2 drops of the solution of sulphocarbonate (prepared by saturating one half of 250 c. c. potash-ley containing 5 p. c. K^2O with hydrogen sulphide, adding the other half, gently warming the liquid for two days with 10 c. c. carbon bisulphide, and then decanting from the uncombined CS^2). If nickel is present, the rose-red or crimson colour will be produced. This reaction suffices to distinguish $\frac{1}{100}$ milligrm. of nickel in 1 c. c. of liquid. The nickel-compound dissolved in the alkaline sulphocarbonate exhibits in dilute solution distinct absorption-bands; concentrated solutions stop the light almost completely (C. D. Braun, *Zeitschr. f. Chem.* [2] v. 309).

For other methods of detecting nickel in presence of cobalt, and for separating the two metals, see COBALT.

NICOTINE. On the preparation of this base see Pribram (*Bull. Soc. Chim.* [2] viii. 276). De Luynes (*Compt. rend.* lxvii. 656) describes a compound of nicotine and orcin, as an oil soluble in excess of narcotine. According to Huber (*Ann. Ch. Pharm.* cxli. 271), nicotine oxidised with potassium chromate and sulphuric acid yields an amidated acid, $C^6H^5NO^2$, from which by distillation with lime an oily base, C^5H^5N, soluble in water is obtained.

NITRATES. 1. **Hydrogen Nitrate** or **Nitric Acid.**—Exact determinations of the specific gravity of aqueous nitric acid of various strengths have been published by J. Kolb (*Ann. Ch. Phys.* [4] x. 136). The percentage *p* of hydrogen nitrate, HNO^3, was determined in each case by adding a weighed and excessive quantity of pure calcium carbonate, and weighing the undissolved portion. The values directly determined are distinguished in the following table by an asterisk:

p	Density		Contraction	*p*	Density		Contraction
	at 0°	at 15°			at 0°	at 15°	
100·00	1·559	1·530	0·0000	58·88	1·387	1·368	0·0861
99·84*	1·559*	1·530*	0·0004	58·00	1·382	1·363	0·0864
99·72*	1·558*	1·530*	0·0010	57·00	1·376	1·358	0·0868
99·52*	1·557*	1·529*	0·0014	56·10*	1·371*	1·353*	0·0870
97·89*	1·551*	1·523*	0·0065	55·00	1·365	1·346	0·0874
97·00	1·548	1·520	0·0090	54·00	1·359	1·341	0·0875
96·00	1·544	1·516	0·0120	53·81	1·358	1·339	0·0875
95·27*	1·542*	1·514*	0·0142	53·00	1·353	1·335	0·0875
94·00	1·537	1·509	0·0182	52·33*	1·349*	1·331*	0·0875
93·01*	1·533*	1·506*	0·0208	50·99	1·341*	1·323*	0·0872
92·00	1·529	1·503	0·0242	49·97	1·334	1·317	0·0867
91·00	1·526	1·499	0·0272	49·00	1·328	1·312	0·0862
90·00	1·522	1·495	0·0301	48·00	1·321	1·304	0·0856
89·56*	1·521*	1·494*	0·0315	47·18*	1·315*	1·298*	0·0850
88·00	1·514	1·488	0·0354	46·64	1·312	1·295	0·0848
87·45*	1·513*	1·486*	0·0369	45·00	1·300	1·284	0·0835
86·17*	1·507*	1·482	0·0404	43·53*	1·291*	1·274*	0·0820
85·00	1·503	1·478	0·0433	42·00	1·280	1·264	0·0808
84·00	1·499	1·474	0·0459	41·00	1·274	1·257	0·0796
83·00	1·495	1·470	0·0485	40·00	1·267	1·251	0·0786
82·00	1·492	1·467	0·0508	39·00	1·260	1·244	0·0755
80·96*	1·488*	1·463*	0·0531	37·95*	1·253*	1·237*	0·0762
80·00	1·484	1·460	0·0556	36·00	1·240	1·225	0·0740
79·00	1·481	1·456	0·0580	35·00	1·234	1·218	0·0729
77·66	1·476	1·451	0·0610	33·86*	1·226*	1·211*	0·0718
76·00	1·469	1·445	0·0643	32·00	1·214	1·198	0·0692
75·00	1·465	1·442	0·0666	31·00	1·207	1·192	0·0678
74·01*	1·462*	1·438*	0·0688	30·00	1·200	1·185	0·0664
73·00	1·457	1·435	0·0708	29·00	1·194	1·179	0·0650
72·39*	1·455*	1·432*	0·0722	28·00*	1·187*	1·172*	0·0635
71·24*	1·450*	1·429*	0·0740	27·00	1·180	1·166	0·0616
69·96	1·444	1·423	0·0760	25·71	1·171*	1·157*	0·0593
69·20*	1·441	1·419*	0·0771	23·00	1·153	1·138	0·0520
68·00	1·435	1·414	0·0784	20·00	1·132	1·120	0·0483
67·00	1·430	1·410	0·0796	17·47*	1·115	1·105	0·0422
66·00	1·425	1·405	0·0806	15·00	1·099	1·089	0·0336
65·07	1·420*	1·400*	0·0818	13·00	1·085	1·077	0·0316
64·00	1·415	1·395	0·0830	11·41*	1·075	1·067*	0·0296
63·59	1·413	1·393	0·0833	7·22*	1·050	1·045*	0·0206
62·00	1·404	1·386	0·0846	4·00	1·026	1·022	0·0112
61·21*	1·400*	1·381*	0·0850	2·00	1·013	1·010	0·0055
60·00	1·393	1·374	0·0854	0·00	1·000	1·999	0·0000
59·59*	1·391*	1·372*	0·0855				

Detection and Estimation of Nitric Acid.—P. Holland (*Chem. News*, xvii. 219) modifies Pelouze's method of estimating nitric acid (by oxidation of a ferrous salt, iv. 87) by performing the oxidation in a vacuum.

Chapman (*Chem. Soc. J.* [2] vi. 172) estimates nitric acid by reducing it with aluminium (a method first suggested by Fr. Schulze, *Jahresb.* 1861, p. 835), and distilling off the ammonia thereby produced. The quantity of ammonia, if somewhat considerable, is determined by titration; if very small, as in ordinary waters, by Nessler's test, the depth of colour produced being compared with that developed in a similar manner in a standard solution of ammonia. (See WATER-ANALYSIS, v. 1032.)

According to E. Schulze (*Zeitschr. anal. Chem.* vi. 379), the estimation of nitric acid by reduction with aluminium (or zinc) is not applicable to vegetable juices, or any liquids containing large quantities of organic matter, whereas that of Schlösing, depending on the reducing action of ferrous chloride (iv. 88), gives good results. Fr. Schulze (*Zeitschr. f. Chem.* [2] iv. 296) now recommends that such liquids be first distilled with dilute potash to remove ammonia, the organic matter then destroyed by heating the alkaline solution with potassium permanganate, the excess of permanganate decomposed with a salt of formic acid, and the nitric acid determined in the neutralised and concentrated filtrate by reduction with aluminium.

Schenk a. Chapman (*Laboratory*, i. 152) find that Pugh's method of estimating nitric acid by converting it into ammonia with stannous chloride, and determining the excess of the latter volumetrically, is not applicable to water-analysis, because organic matters of all kinds likewise convert stannous into stannic chloride, ammonia being also formed if the organic matter is nitrogenous.

C. Nöllner (*Zeitschr. anal. Chem.* vi. 375; vii. 355) estimates nitric acid in saltpetre and saltpetre-lyes by means of the solubility of ammonium nitrate in alcohol. 1 grm. of the salt is heated with ammonium sulphate and a little water; absolute alcohol is then added; and the liquid filtered from the sulphates is mixed with an alcoholic solution of pure potash, whereby potassium nitrate is precipitated, and may be washed with alcohol and weighed.

The following process for the *detection* of nitric and nitrous acids, founded on an observation of Hofmann (*Ann. Ch. Pharm.* xlvii. 60), is given by C. D. Braun (*Zeitschr. anal. Chem.* vi. 71): 1 c. c. of pure strong sulphuric acid is mixed on a watch-glass by drops with ½ c. c. of a solution of *aniline sulphate*, and a drop of the liquid to be tested is brought on the end of a glass rod to the edge of the acid liquid. If only a trace of the nitric acid is present, deep carnation-red streaks and curves make their appearance as the liquids slowly mix, and the entire liquid becomes rose-red, or, if the quantity of nitric acid is rather larger, carmine-red to brown-red or brown-yellow. In this manner nitric acid may be detected in common sulphuric acid and in spring or river water.

On the reduction of nitric acid by tin and hydrochloric acid, see HYDROXYLAMINE (p. 722).

According to Schönbein (*J. pr. Chem.* cv. 208; *Jahresb.* 1868, p. 179), those organic substances which decompose hydrogen dioxide catalytically have also the power of reducing nitrates in solution to nitrites, and completely decomposing the latter. This reaction has been especially noticed with fresh confervæ, yeast, and fungi in general, also with blood-corpuscles.

2. **Metallic Nitrates.** *Copper Nitrates.*—A *tetracupric salt*, $4CuO.N^2O^5 + 3\frac{1}{2}H^2O$, is precipitated from a boiling solution of the normal nitrate by an acetate of alkali-metal, magnesium, manganese cobalt, nickel, zinc, cadmium, copper, or lead, also by many propionates and valerates, also on mixing a solution of cupric acetate with the nitrates of many of the bases just mentioned; ammonium nitrate gives no precipitate (Casselmann, *Jahresb.* 1865, p. 274).

Indium Nitrate.—See INDIUM (p. 732).

Iron Nitrates.—*Ferrous nitrate* is most readily prepared by dissolving ferrous sulphide in cooled nitric acid of sp. gr. less than 1·12. The solution, made as neutral as possible, carefully concentrated by evaporation, and then exposed to a winter temperature, deposits the salt in crystals, which appear to consist of $(NO^3)^2Fe + 6H^2O$. These crystals may be preserved in the moist state at low temperatures; but when separated from the mother-liquor they are quickly converted into red-brown basic ferric nitrate. 100 pts. of the crystallised salt dissolve in 50 pts. water at 0°, in 40·8 pts. at 15° (sp. gr. of solution 1·48), and in 33·3 pts. at 25° (sp. gr. of solution 1·50 (Ordway, *Sill. Am. J.* [2] xl. 325).

Cubic *ferric nitrate*, $Fe^2O^3.3N^2O^5 + 12H^2O$ or $(Fe^2)^{vi}(NO^3)^6 + 12H^2O$, is always obtained when the solution is so composed that it may be regarded as containing equivalent quantities of the crystallised salt and the hydrate of nitric acid, $N^2O^5.3H^2O$. If it contains less water, no crystals are formed; if more, the cubic salt is always associated with the clinorhombic salt, containing $18H^2O$ (iv. 93). The latter is formed exclusively when the solution has a constitution represented by the formula $(Fe^2O^3.3N^2O^5 + 18H^2O) + n(N^2O^5.4H^2O)$. The cubic salt also crystallises out when the clinorhombic salt is heated till it has lost 14 p. c., and the liquid is mixed with an equal volume of fused hydric nitrate, (NO^3H), or when 1 mol. of the fused clinorhombic salt is mixed with rather more than 4 mol. NO^3H. During the cooling and crystallisation the liquid must be protected from atmospheric moisture (Ordway).

The same method serves also for the preparation of other nitrates in the crystalline state, especially those of *chromium*, *glucinum*, *zinc*, and *manganese*; the glucinum salt crystallises in quadratic octohedrons (Ordway).

On commercial nitrate of iron, see Lenssen (*Zeitschr. f. Chem.* [2] vi. 284).

Lead Nitrates.—The *diplumbic salt*, $Pb(NO^3)^2.PbO + 4H^2O$, is precipitated from a solution of potassium nitrate or normal lead nitrate by a slight excess of basic lead acetate. The *triplumbic salt*, $Pb(NO^3)^2.2PbO$, is formed by mixing the aqueous solutions of triplumbic acetate and potassium nitrate (the precipitate redissolves in excess of the basic acetate); it is slightly soluble in cold water, more soluble than the diplumbic salt, is precipitated therefrom in the crystalline form by alcohol, and crystallises from the hot-saturated solution in small hard prisms. It has been obtained with quantities of water varying from 1 to ½ mol. The *sexplumbic salt*, $Pb(NO^3)^2.5PbO + H^2O$, is separated from the solution of either of the preceding salts by excess of ammonia, as a fine white perfectly insoluble precipitate (J. Löwe, *Zeitschr. anal. Chem.* iv. 388; *J. pr. Chem.* xcviii. 385).

Sodium Nitrate. $NaNO^3$.—This salt occurs native, not in Chile, as commonly stated, but in the province of Tarapaca, Dep. Moquegua, in Peru. The following analyses are by D. Forbes (*Phil. Mag.* [4] xxxii. 139): *a.* Comparatively pure selected crystals from the bed of La Noria, about 30 miles east of Iquique, and 3052 feet above the sea-level.—*b.* Fine-grained saline mass from a hill on the Sal de Ohispo, west of the port of Pisagua:

$NaNO^3$	NaCl	$CaCl^2$	KI	Na^2SO^4	$MgSO^4$	$Al^2(SO^4)^3$	Insol.		
76·69	21·63	0·45	—	0·92	—	—	0·31	=	100
21·01	55·27	0·33	0·87	4·74	5·93	9·81	2·04	=	100

Thallium Nitrates.—See THALLIUM (v. 754, 756). According to Carstanjen (*Jahresb.* 1867, p. 280), thallious nitrate is decomposed at a bright red heat, giving off a volatile thallium-compound, and leaving a mixture of thallious nitrite and thallic oxide.

3. **Nitric Ethers** (Chapman a. Smith, *Chem. Soc. J.* [2] v. 576; vi. 174).—*Amyl Nitrate*, $C^5H^{11}NO^3$, is best prepared by gradually pouring 150 c. c. of a mixture of 1 vol. nitric acid (sp. gr. 1·36) and 3 vol. strong sulphuric cooled with ice and salt into 50 c. c. amyl alcohol, through a funnel reaching to the bottom of the vessel, the liquid being stirred all the while. The amyl nitrate then rises to the surface as an oily layer, which may be purified by washing with weak potash-ley and water, drying over calcium chloride, and rectification.

It boils constantly at 147°–148°; between 7° and 8° it has exactly the same specific gravity as water, but is lighter above and heavier below that temperature. The inhalation of its vapour produces headache and restlessness for several hours. It is quite insoluble in water, soluble in ethylic, methylic, and amylic alcohols, benzol, and glacial acetic acid, insoluble in concentrated formic acid, hydrochloric acid, cold nitric and sulphuric acids, and is not attacked by hydrochloric, acetic, formic, or oxalic acid, even at the boiling heat. At its boiling point it dissolves considerable quantities of sulphur and phosphorus. It is not attacked by trichloride or pentachloride of phosphorus; but with the oxychloride it gives off hydrochloric acid, and forms chlorinated substitution-products of intolerable odour. With sodium methylate and alcoholic potash it behaves like amyl nitrite (p. 870). Sodium introduced into well-cooled amyl nitrate acquires a strong silvery lustre, and forms, with violent reaction, sodium amylate and sodium nitrate: $C^5H^{11}NO^3 + Na^2 = C^5H^{11}NaO + NaNO^2$. If the amyl nitrate is diluted with an equal volume of ether, sodium acts very violently on it, even in the cold.

Amyl nitrate is not acted upon by *zinc-ethyl* when the two are mixed in an atmosphere of carbon dioxide; but on bringing the mixture for a moment in contact with the air, it explodes with vivid incandescence. If heated to about 40° it explodes with extraordinary violence. By dilution with ether the reaction may be moderated; it then begins at about 100°, yielding products of deep decomposition.

Ethyl Nitrate, $C^2H^5NO^3$, may be prepared like the amyl compound, and reacts in a similar manner with the chlorides of phosphorus; it likewise dissolves sulphur and phosphorus, and is decomposed by potassium acetate into ethyl acetate and potassium nitrate; with sodium it forms ethylate and nitrate of sodium.

Methyl Nitrate resembles the ethyl compound, distils over sodium without alteration, and is decomposed by it only when the two are heated together in a sealed tube and in presence of ether.

On the nitrates of isobutyl and isopropyl see BUTYL and PROPYL COMPOUNDS.

On the reduction of nitric ethers by tin and hydrochloric acid, see HYDROXYLAMINE (p. 722).

Action of Fatty Acids on Nitric Ethers in Presence of Sulphuric Acid.—When amyl nitrate is added by drops to a warm mixture of 20 pts. glacial acetic acid and 1 pt. strong sulphuric acid, carbon dioxide and methyl nitrite are given off, while amyl acetate remains in solution:

$$C^5H^{11}NO^3 + 2C^2H^4O^2 = C^5H^{11}.C^2H^3O^2 + CH^3NO^2 + CO^2 + H^2O.$$

Butyl nitrate and ethyl nitrate act in a similar manner. With methyl nitrate the reaction appears to be as follows:

$$3CH^3NO^3 = 2CH^3NO^2 + HNO^3 + CO^2 + H^2O.$$

Similar reactions are also produced when valeric acid is used instead of acetic acid, but the butyl nitrite thereby produced suffers immediate decomposition. Amyl nitrate and formic acid in presence of sulphuric acid yield amyl formate, nitrogen monoxide, carbon dioxide, and water, red vapours being also given off.

NITRILES. See CYANIDES, ALCOHOLIC (pp. 522–528).

NITRITES. For the preparation of *potassium nitrite*, Stahlschmidt (*Pogg. Ann.* cxxviii. 466; *Jahresb.* 1866, p. 153) recommends the following process, founded on the fact that potassium nitrate in presence of free alkali is quickly reduced by the action of zinc-powder, even at ordinary temperatures, to nitrite, and partly to caustic potash, with evolution of nitrogen. A solution of potassium nitrate saturated at 30°–40° is mixed with about one-tenth of its volume of aqueous ammonia; and zinc-powder is added by small portions, with frequent agitation and cooling, to keep the temperature below 50°, till the greater part of the nitrate is decomposed (which may be known by a sample of the liquid, boiled to expel ammonia and filtered from precipitated zinc oxide, no longer giving a perceptible precipitate when mixed with 4 or 5 vol. alcohol). The clarified solution is then decanted from the zinc, boiled to volatilise the ammonia, then filtered, and treated with carbon dioxide at the boiling heat to decompose the metallic nitrites. The solution thus freed from zinc and cadmium is lastly neutralised with nitric acid, and the potassium nitrate is separated by evaporation and crystallisation. A similar process may be applied to the preparation of other nitrites. Erdmann (*Jahresb.* 1866, 154) prepares potassium nitrite by melting saltpetre in a cast-iron crucible at a moderate red heat, with several times its weight of iron filings or turnings, till a sample dissolved in water and treated with sulphuric acid gives off abundance of nitrous acid. The cooled mass is then lixiviated with water; the solution somewhat concentrated till the undecomposed nitrate crystallises out, then supersaturated with nitrous acid (evolved from starch and nitric acid), and evaporated at a gentle heat.

Nitrites of Nickel and Cobalt (Erdmann, *J. pr. Chem.* xcvii. 385; *Jahresb.* 1865, p. 717; 1866, p. 245).—Nickel solutions quite free from cobalt or calcium yield on addition of a large quantity of potassium nitrite, a red-brown precipitate of potassium-nickel nitrate (iv. 74); but when calcium chloride is added to a solution of this double salt, or to a mixture of nickel chloride and potassium nitrite, a yellow crystalline precipitate of the triple salt, $NiCaK^2(NO^2)^6$, is formed, very slightly soluble in cold water, but dissolving easily, with green colour, in boiling water. Barium chloride and strontium chloride form in like manner yellow or reddish-yellow triple salts of analogous constitution, which separate from hot solutions in microscopic cubes or combinations of the cube with octohedral faces. Cobalt salts mixed with chloride of barium, strontium, or calcium, yield with potassium nitrite blackish-green precipitates of corresponding composition; they are formed, however, only in concentrated solutions, and decompose during filtration and washing. It appears from these results that the separation of nickel from cobalt by potassium nitrite (i. 1045) cannot be effected in presence of calcium salts.

A neutral solution of cobalt chloride forms with excess of potassium nitrite a yellow crystalline precipitate of the salt $3NiK^2(NO^2)^4 + H^2O$; a solution mixed with a large excess of acetic acid yields double salts of more complex constitution.

Tetrammonio-nickel Nitrite, $4NH^3.Ni(NO^2)^2$, is gradually deposited from a mixture of nickel acetate and ammonium nitrite in small, shining, cherry-red, apparently monoclinic crystals. A double salt of tetrammonio-cobaltic nitrite with potassium nitrite, $4NH^3.Co^2(NO^2)^6 + 2KNO^2$, is obtained by mixing a solution of cobalt chloride with a large quantity of sal-ammoniac and excess of potassium nitrite; the liquid then deposits at a gentle heat shining yellow scales of potassium-cobalt nitrite, and afterwards brown vitreous rhombic prisms of the double salt just mentioned. The potassium in this salt may be replaced by equivalent quantities of other metals: thus its solution forms with silver nitrate a yellow or orange-coloured precipitate of the salt $4NH^3.Co^2(NO^2)^6 + 2AgNO^2$. A neutral solution of cobalt chloride mixed with neutral ammonium nitrite yields by slow evaporation brown rhombic prisms of the double salt $4NH^3.Co^2(NO^2)^6 + 2NH^4NO^2$.

On the estimation of nitrous acid by means of potassium permanganate, see Kübel (*J. pr. Chem.* cii. 222; *Zeitschr. f. Chem.* [2] iv. 314).

Nitrous Ethers. *Amyl nitrite*, $C^5H^{11}NO^2$, is formed, together with nitric acid, by the action of nitrogen tetroxide on amyl alcohol:

$$C^5H^{12}O + N^2O^4 = C^5H^{11}NO^2 + NHO^3.$$

When nitrous acid vapour (from starch and nitric acid) is passed into amyl alcohol, ammonium nitrate is produced, as well as amyl nitrite, probably because the nitrous acid vapour is a mixture of [or is resolved into] the tetroxide and dioxide of nitrogen:

$$5C^5H^{12}O + 3N^2O^3 = 5C^5H^{11}NO^2 + NH^3 + H^2O$$

(N. Bunge, *Zeitschr. f. Chem.* [2] ii. 82, 225; *Bull. Soc. Chim.* [2] vi. 482).

Amyl nitrite added by drops to a hot mixture of *potassium dichromate* and *dilute sulphuric acid* is oxidised to nitric acid, valeric acid, and amyl valerate. Strong sulphuric acid acts violently on it, sometimes setting it on fire; sulphuric acid diluted with 2 pts. water decomposes it at 100°, forming sulphurous oxide, nitrogen dioxide, and amyl valerate:

$$2C^5H^{11}NO^2 + H^2SO^4 = 2H^2O + SO^2 + N^2O^2 + C^5H^{11}.C^5H^9O^2.$$

Amyl nitrite dropped into a gently warmed mixture of concentrated *hydriodic acid* and *phosphorus* is decomposed, with formation of nitrogen dioxide and amyl iodide. Treated with excess of *phosphoric anhydride*, it is violently attacked, forming a brown solid mass, probably containing the cyanide of an alcohol-radicle of the allyl series, $C^4H^7.CN$, formed according to the equation $C^5H^{11}NO^2 = C^5H^7N + 2H^2O$ (Chapman, *Chem. Soc. J.* [2] iv. 333, 336).

Amyl nitrite (boiling at 98°–99°) heated to 106° with *sodium methylate* is resolved into methyl-amyl oxide and sodium nitrite:

$$C^5H^{11}NO^2 + CH^3NaO = CH^3.C^5H^{11}.O + NaNO^2.$$

With *sodium ethylate*, it yields in like manner, ethyl-amyl oxide; with an alcoholic solution of potash, it forms amyl alcohol and ethyl-amyl oxide in proportions varying with the quantity of water present. Heated with *ammonia* to 130°, it is resolved into amyl alcohol, nitrogen, and water:

$$C^5H^{11}NO^2 + NH^3 = C^5H^{12}O + N^2 + H^2O.$$

Strong aqueous *hydrochloric acid* decomposes it only when heated, and even then not completely; but when saturated with hydrochloric acid gas and heated, it yields amyl alcohol, nitrogen dioxide, and chlorine:

$$C^5H^{11}NO^2 + HCl = C^5H^{12}O + NO + Cl;$$

if water is altogether absent, amyl chloride and its chlorinated derivatives are also formed. With *hydrobromic acid*, amyl bromide and nitrous acid are formed: $C^5H^{11}NO^2 + HBr = C^5H^{11}Br + HNO^2$; with *hydriodic acid*, iodine is separated, and ammonia is frequently formed:

$$2C^5H^{11}NO^2 + 4HI = 2C^5H^{11}I + N^2O^2 + 2H^2O + I^2.$$

Boiled with *glacial acetic acid*, it gives off red vapours, then pure nitrogen dioxide, and forms amyl acetate:

$$C^5H^{11}NO^2 + C^2H^4O^2 = C^5H^{11}.C^2H^3O^2 + HNO^2.$$

Heated with *formic acid*, it reacts according to the equation:

$$2C^5H^{11}NO^2 + 4CH^2O^2 = 2(C^5H^{11}.CHO^2) + N^2O + 2CO^2 + 3H^2O.$$

Heated with a concentrated solution of *zinc chloride*, it gradually dissolves, with abundant evolution of gas and formation of valeraldehyde and amyl valerate:

$$4C^5H^{11}NO^2 - 2H^2O = 4C^5H^{10}O + N^2O^3 + N^2;$$

and

$$4C^5H^{11}NO^2 - 2H^2O = 2(C^5H^{11}.C^5H^9O^2) + N^2O^2 + N^2.$$

Zinc acts but slowly on amyl nitrite at the boiling heat, forming zinc amylate, with continuous evolution of nitrogen dioxide:

$$2C^5H^{11}NO^2 + Zn = Zn(C^5H^{11}O)^2 + N^2O^2.$$

Sodium acts but slowly at first on amyl nitrite, but the reaction quickly becomes violent and sometimes explosive; if the liquid be sufficiently diluted with ether, the action goes on more quickly, with evolution of nearly pure nitrogen if the sodium is in excess, chiefly of nitrogen monoxide in the contrary case, and formation of amylate and oxide of sodium, but only a small quantity of nitrite:

$$2C^5H^{11}NO^2 + 3Na^2 = 2C^5H^{11}NaO + 2Na^2O + N^2;$$

and

$$2C^5H^{11}NO^2 + 2Na^2 = 2C^5H^{11}NaO + Na^2O + NO$$

(Chapman a. Smith, *Chem. Soc. J.* [2] v. 576).

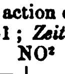
NITRO-COMPOUNDS. On the formation and general properties of organic compounds formed from others by substitution of NO^2 for H, see Engelhardt a. Latschinoff (*Zeitschr. f. Chem.* [2] vi. 225).

NITROGEN OXIDES. *Monoxide.* N^2O.—According to R. Weber (*Berl. Akad. Ber.* 1866, 588; *Jahresb.* 1866, p. 140), both nitrous and nitric acids are reduced to nitrogen monoxide by the action of sulphurous acid. The monoxide is also produced, though very slowly, by the action of sulphurous acid on the dioxide, as formerly observed by Pelouze. Nitrogen monoxide is sometimes formed in sulphuric acid chambers, giving rise to loss of nitric acid and disturbance of the process. It is formed chiefly from the nitrous acid (and to a less extent from the nitric acid) when this acid is in contact with excess of sulphurous acid and a large quantity of water. This reduction may therefore be avoided by the introduction of a sufficient quantity of nitric acid, and by having a certain quantity of dilute sulphuric acid (which also interferes with the reduction) constantly present in the chamber.

Salts of Nitrogen Monoxide, or *Hyponitrites*, are formed by the action of sodium-amalgam on the nitrates of the alkali-metals. The sodium salt is alkaline to test-paper, and gives with silver nitrate a yellow precipitate having the composition NOAg (Divers, *Proc. Roy. Soc.* xix. 425; *Chem. Soc. J.* [2] ix. 484).

Dioxide. NO or N^2O^2.—According to Chapman (*Chem. Soc. J.* [2] v. 166), this oxide is slowly reduced by concentrated hydriodic acid, with formation of ammonia and separation of iodine. It is oxidised by permanganates to nitric acid, with separation of manganese dioxide if the solution is neutral. The trioxide and tetroxide are oxidised to nitric acid in the same manner, but the monoxide is not attacked.

Trioxide. N^2O^3.—On the action of water on this compound and on nitrous acid, see Frémy (*Compt. rend.* lxx. 61; *Zeitschr. f. Chem.* [2] vi. 138).

Tetroxide. NO^2 or N^2O^4 =  $\begin{matrix}NO^2\\|\\NO^2\end{matrix}$.—Deville a. Troost (*Compt. rend.* lxiv. 257; *Jahresb.* 1867, p. 177) have determined the vapour-density of this compound by Dumas' process for temperatures above its boiling point. To obtain a series of determinations for increasing temperatures, the water-bath, or oil-bath for temperatures above 100°, was heated by a gas-flame 5° to 10° higher in each experiment than in the preceding; the glass globe of the capacity of 84·68 cub. cent. was immersed in the bath with its point still unbroken; kept in it about half an hour at a uniform temperature; then opened carefully and without loss; sealed again after the escape of gas had ceased; then weighed, &c. &c. The results of the experiments are given in the following table, in which P denotes the weight of the vapour contained in the globe at the variable temperature t; K the expansion-coefficient of the glass; β the expansion-coefficient of nitrogen tetroxide between two successive values of t, and therefore $\frac{v(1+kt)}{P}$ the volume occupied by 1 gram of vapour at $t°$; D denotes the density calculated on the assumption that nitrogen tetroxide is a perfect gas, so that $\beta = 0·00367$, the normal coefficient of expansion, and that the density varies with the pressure according to Mariotte's law:

Vapour-density of Nitrogen tetroxide.

t	D	P	$\frac{v(1+kt)}{P}$	$100\,\beta$
26·7°	2·65	2·604	320·36	
35·4	2·53	2·419	345·12	0·888
39·8	2·46	2·358	360·42	1·008
49·6	2·27	2·108	403·33	1·215
60·2	2·08	1·870	454·95	1·207
70·0	1·92	1·688	505·85	1·137
80·6	1·80	1·530	556·37	0·946
90·0	1·72	1·426	597·22	0·721
100·1	1·68	1·354	629·23	0·531
111·3	1·65	1·291	660·29	0·441
121·5	1·62	1·240	688·74	0·422
135·0	1·60	1·180	723·87	0·378
154·0	1·58	1·118	764·40	0·367
183·2	1·57	1·037	824·77	

The coefficient β exhibits a maximum value at the temperature of 40°, and does not become constant till the temperature rises above 100°.

The nitrogen tetroxide with which the preceding experiments were made was prepared by direct combination of the dioxide with pure oxygen. It solidified constantly at −10°, but when once fused remained liquid even at −21·3°. The yellow colour of the liquid and vapour becomes darker as the temperature rises; at 22° the gas is reddish, and at 183° rather black than red.

Deville a. Troost infer from their experiments that the vapour-density of nitrogen tetroxide is constant and equal to 1·589, and therefore that the quantity represented by the formula NO^2 occupies 2 volumes ($= H^2$).

Salet, on the other hand (*Compt. rend.* lxvii. 488; *Jahresb.* 1868, p. 177), adduces an experimental argument in favour of the view that at comparatively low temperatures the quantity of the vapour of nitrogen tetroxide contained in two volumes is N^2O^4, and that as the temperature rises, the compound is more and more resolved into two molecules, NO^2, each occupying two volumes. Firstly, from the relations

$$a + b = D; \qquad \frac{a}{23} + \frac{b}{46} = 1,$$
$$a = 46 - D; \qquad b = 2D - 46$$

(in which D is the density of the mixed vapour referred to hydrogen as unity, a and b the quantities by weight of NO^2 and N^2O^4 contained in it, 23 the theoretical density of NO^2, 46 that of N^2O^4), he calculates, from the vapour-densities determined by Deville and Troost, the amount of dissociation at the various observed temperatures, according to the formula $\frac{a}{D}$, which expresses the weight of NO^2 contained in the unit of vapour. Secondly, assuming that the vapour of N^2O^4 is colourless, and that of NO^2 coloured, he calculates the lengths which a column of the vapour at 26·7° must have in order to exhibit a depth of colour equal to that of a column of constant length regarded as unity at the temperatures given in the following table. On the other hand, having ascertained that a short hot column and a longer cold column of the vapour, which exhibit equal depths of colour, also exhibit similar absorption-spectra, he determines the required lengths of the columns by a peculiar mode of observation. The near agreement of the experimental results thus obtained with theory is exhibited in the following table, in which the column headed 'Calculated lengths' contains the values obtained by the formula $x = \frac{a}{D} \cdot \frac{P}{3{\cdot}1214 \times 20{\cdot}26}$ (P denoting the weight of the unit of volume at 1°):

Temperature	A Weight P of a litre of vapour	$\frac{a}{D}$	B Lengths of Column	
			calculated	observed
26·7°	3·1214	20·26 p. c.	1	1
35·4	2·8975	25·8	1·182	1·18
39·8	2·7745	29·6	1·299	1·28
49·6	2·4793	40·5	1·588	1·28
60·2	2·1980	53·3	1·852	1·9
70·0	1·9768	66·1	2·066	1·9
80·6	1·7973	76·9	2·185	2·2
90·0	1·6744	85·1	2·253	2·2
100·1	1·5892	89·7	2·254	2·3
111·3	1·5144	93·3	3·234	2·25
121·5	1·4519	96·6	2·218	2·24
135·0	1·3814	99·1	2·165	2·20
154·0	1·3082	101·7 *	2·104	2·12
200·0			1·9	1·95
225·0			1·8	1·95
250·0			1·7	1·95
275·0			1·6	1·6
300·0			1·56	1·52

These numbers show that the depth of colour increases rapidly with the temperature at first, attains a maximum when the decrease of density balances the increase of coloration, and afterwards diminishes when the diminution of the density exerts a predominating influence.

A. Naumann (*Ann. Ch. Pharm. Suppl.* vi. 203) has also calculated, from the experimental results of Deville and Troost, the amount of dissociation of the molecule N^2O^4 which may be supposed to take place at the several temperatures observed. The calculations are based upon the formula

$$p = \frac{100(d-D)}{(a-1)D},$$

in which *d* is the theoretical specific gravity of a body susceptible of dissociation, D the observed sp. gr. of the gaseous mixture at any temperature, *a* the number of molecules into which a molecule of the original compound is resolved by dissociation, and *p* the number of parts per cent. of the dissociated compound.

Temperature	Vapour-density of Nitrogen tetroxide	Percentages of Decomposition	Increase per. cent. of decomposition for temperature intervals of 10°
26·7°	2·65	19·96	
35·4	2·53	25·65	6·5
39·8	2·46	29·23	8·1
49·6	2·27	40·04	11·0
60·2	2·08	52·84	12·1
70·0	1·92	65·57	13·0
80·6	1·80	76·61	10·4
90·0	1·72	84·83	8·8
100·1	1·68	89·23	4·4
111·3	1·65	92·67	3·1
121·5	1·62	96·23	3·5
135·0	1·60	98·69	1·8
154·0	1·58		
183·2	1·57		

These numbers afford an explanation of the apparent maximum of the expansion-coefficient observed by Deville and Troost, inasmuch as they exhibit a dissociation of the vapour gradually increasing with the temperature.

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* Corresponding to the somewhat too low density observed.

On the spectra of the vapours of nitrogen trioxide and tetroxide, see Luck (*Zeitschr. f. Chem.* [2] vi. 287).

Pentoxide or *Nitric Anhydride.* N^2O^5.—This oxide is most readily prepared by passing the vapour of nitryl chloride, NO^2Cl, over well-dried silver nitrate heated to 60°–70°, and condensing the product by a freezing mixture. The anhydride then collects in colourless prismatic or needle-shaped crystals having exactly the properties described by Deville (Odet a. Vignon, *Compt. rend.* lxix. 1142; *Zeitschr. f. Chem.* [2] vi. 81).

NITROSO-COMPOUNDS. The formation of these compounds by the action of nitrous acid on azotised bodies appears to depend essentially on the presence of the imidogen group NH in the latter, the reaction consisting in an interchange between the group NO of the nitrous acid and the H of the imidogen; thus:

$$R.NH + NO.OH = HOH + RN.NO$$

(Baeyer, *Zeitschr. f. Chem.* [2] vi. 215).

NITRYL CHLORIDE, NO^2Cl, is produced by the action of phosphorus oxychloride on lead nitrate, or better on silver nitrate. It is a liquid having a faint yellow colour, boiling at + 5°, remaining liquid at −31°, and converted by water into nitric and hydrochloric acids (Odet a. Vignon).

NONANE or **NONYL HYDRIDE,** C^9H^{20}, is produced by heating cumene, C^9H^{12}, with 80 pts. of saturated aqueous hydriodic acid (Berthelot); also, according to H. Vohl (*Jahresb.* 1865, p. 841), when tetradecane, $C^{14}H^{30}$, is passed through red-hot wrought-iron tubes.

NONYLENE, C^9H^{18}, is found among the hydrocarbons produced by decomposition of the lime-soap of Menhaden oil (p. 814). Boiling point, 253° (Warren a. Storer).

NUCITANNIN or **NUCITANNIC ACID.** A peculiar tannin occurring in the episperm of walnuts. It dissolves in water and alcohol, is precipitated by basic lead acetate, and is resolved by dilute acids into sugar and a red acid substance, *rufic acid*, soluble in ammonia and in alcohol. The nucitannin is likewise accompanied by considerable quantities of gallic and ellagic acids, which greatly impede its purification. *Rufic acid* is a brown-red amorphous substance easily soluble in alcohol, forming soluble salts with the alkali-metals, insoluble or slightly soluble coloured salts with calcium, lead, and silver (Phipson, *Chem. News*, xx. 116).

NUTRITION. Frankland (*Phil. Mag.* [4] xxxii. 182; *Chem. Soc. J.* [2] vi. 33) has determined the heat of combustion of muscular substance, urea, and other substances which play an essential part in the transformation of tissue in the animal body, by burning them with a mixture of potassium chlorate and manganese dioxide. The mean results are as follows:

1 gram of substance dried at 100°	developed by combustion	
	Heat-units	Corresponding units of force: Metre-kilograms
Beef-muscle, purified by repeated washing with ether	5103	2161
Purified albumin	4998	2117
Beef-fat	9069	3841
Hippuric acid	5383	2280
Uric acid	2615	1108
Urea	2206	934

Dried muscle and albumin, in passing through the organism, yield about a third of their weight of urea. Hence it may be calculated that these substances, when oxidised in the animal body, yield the following amounts of heat and force:

	Heat-units	Metre-kilograms
Beef-muscle	4368 .	1848
Albumin	4263 .	1803

Frankland has also determined the quantities of heat produced by the combustion of various articles of food with potassium chlorate. The following table gives the mean values in heat-units for 1 gram of the undried substances, together with the mechanical equivalents in metre-kilograms:

1 gram of undried substance	Water p. c.	Develops when burnt in oxygen		When oxidised in the animal body.
		Heat-units	Met-kil. of force	Met-kil. of force
Cheshire cheese	24	4647	1969	1846
Potatoes	73	1013	429	422
Apples	82	660	280	273
Oatmeal	—	4004	1696	1665
Wheat-flour	—	3936	1669	1627
Pea-meal	—	3936	1667	1598
Ground rice	—	3813	1615	1591
Arrowroot	—	3912	1657	1657
Bread-crumb	44	2231	945	910
Bread-crust	—	4459	1888	—
Beef (lean)	70·5	1567	664	604
Veal	70·9	1314	556	496
Ham (boiled)	54·4	1980	839	711
Mackerel	70·5	1789	758	335
Whiting	80·0	904	383	—
White of egg	86 3	671	284	244
Hard-boiled egg	62·3	2383	1009	966
Yolk of egg	47	3423	1449	1400
Milk	87	662	280	266
Carrots	86	527	223	220
Cabbage	88·5	434	184	178
Cocoa-nibs	—	6873	2911	2902
—	—	9069	3841	
Butter	—	7264	3077	
Cod-liver oil	—	9107	3857	
Lump-sugar	—	3348	1418	
Commercial grape-sugar	—	3277	1388	
Bass's ale (alcohol reckoned)	88·4	775	328	
Guinness's stout	88·4	1076	455	

The question as to how far the production of muscular force depends on the oxidation of nitrogenous materials, has been examined experimentally by Fick a. Wislicenus (*Phil. Mag.* [4] xxxi. 485). These observers estimated the quantities of albuminous substances oxidised in their own bodies, on a purely non-nitrogenous diet, both at rest and during muscular exertion (in an ascent of the Faulhorn), taking as a measure of this oxidation the amount of nitrogen excreted in the urine. These amounts were as follows: (*a*) During 11 hrs. 50′ rest, previous to the ascent; (*b*) during the ascent, 3 hrs. 10′; (*c*) during 5 hrs. 40′ rest after the ascent; (*d*) during the following 11 hrs. (night) after a full meat diet. The numbers marked I. give the results for Fick (weighing 66 kilograms); those marked II. for Wislicenus (76 kilograms):

		Urea	Amount of nitrogen in the urea	Amount of Nitrogen in the Urine		Corresponding quantity of albuminoids oxidised [*]
				Total	Per hour	Total
a	I.	12·4820	5·8249	6·9153	0·63	46·1020
	II.	11·7614	5·4887	6·6841	0·61	44·5607
b	I.	7·6330	3·2681	3·3130	0·41	22·0867
	II	6·6973	3·1254	3·1336	0·39	20·8907
c	I.	5·1718	2·4151	2·4293	0·40	16·1953
	II.	5·1020	2·3809	2·4165	0·40	16·1100
d	I.			4·8167	0·45	32·1113
	II.			5·3462	0·51	35·6413
b + *c*	I.			5·7432		37·1700
	II.			5·5501		37·0007

[*] Calculated on the assumption that albuminoids contain 15 p. c. N.

The quantities of albuminoïds oxidised during the ascent of the mountain (1956 metres high) were therefore: I. 37·17 grms., and II. 37·0 grms. Comparing these numbers with Frankland's estimate of the amount of force generated by the oxidation of 1 gram of albumin, we obtain, for I. 68,690 metre-kilograms, for II. 688,376 metre-kilograms of force generated during the ascent by the oxidation of albuminous substances in the body.

Further, Fick and Wislicenus conclude—from calculations for which we must refer to their memoir—that the work expended in raising the body through the height of 1956 metres, and in the action of the heart and respiratory organs during the same time (neglecting that expended in other bodily movements), was for I. 159,637, and for II. 184,287 metre-kilograms. Since, however, of the total energy generated in a given time by the process of oxidation in the organism, only a fraction is expended in mechanical force—this fraction, according to Haidenhain, not exceeding one-half in the most favourable case—these values must be doubled in order to obtain the total amount of energy developed by the oxidising process. We have then as the final result:

	I. Metre-kilograms.	II. Metre-kilograms.
Maximum expenditure of force during the ascent . . .	319,274	368,574
Maximum of force generated by oxidation of muscular substance	68,690	68,376

Hence it appears that the force generated by the oxidation of muscle amounts to only a fifth of that required for the work actually performed, and consequently that the greater part of the muscular force is generated by the non-azotised constituents (fats, carbohydrates) of the animal body (or of the food). A certain quantity of the muscular substance is however oxidised at the same time, and this oxidation gives rise to the nitrogenous constituents of the urine. These views afford an explanation of the fact that during muscular exertion the amount of carbonic acid eliminated is enormously increased, whereas the quantity of nitrogen in the urine exhibits little or no increase (see table, p. 875); also of the necessity for a complicated digestive apparatus in the herbivora, to effect the transformation of the greatest possible quantity of cellulose (Fick a. Wislicenus).

Nitrogenous food serves chiefly for the renewal of the muscular substance, although it may also contribute to the development of muscular and nervous power. The muscle may be regarded as a mechanism for converting latent energy into mechanical force, and this force is produced mainly by the oxidation of substances introduced into the blood, not by that of the muscle itself: its production is necessarily accompanied by development of heat, and this is perhaps the only source of animal heat. The muscle, like every other part of the body, is continually renewed, but this renewal does not stand in any direct relation to its function, inasmuch as it is not perceptibly greater during strong exertion than during comparative rest (Frankland).

The connection between the elimination of nitrogen and the development of muscular energy has also been made the subject of an extended series of experiments by Dr. Parkes (*Proc. Roy. Soc.* xv. 339; xvi. 44), the mean results of which are as follows: 1. With a regular addition of nitrogen in the food, the nitrogenous excretion increases slightly during rest as compared with a period of ordinary exercise.—2. The urinary nitrogenous excretion decreases during active exercise as compared with a period of rest, and this decrease is perceptible both when the ingress of nitrogen is stopped, as well as when the nitrogen is supplied in regular amount.—3. After exercise there is an excess, though not great, in the nitrogenous excretion.—4. Nitrogen, when again supplied after having been cut off, is retained in the system after both rest and exercise, and in greatest amount in the latter case, showing that it is needed in the system, and that an insufficient supply must be subsequently compensated.

From these results Parkes concludes that the muscle during its activity takes up nitrogen, and that, parallel with the assimilation of nitrogen, and as a consequence of it, the decomposition of the non-nitrogenous substance surrounding the muscular tissue takes place, which, according to Fick and Wislicenus, is the source of the muscular energy. In the subsequent period of rest, the products of metamorphosis are removed, and the muscle at the same time loses nitrogen. Nitrogen is therefore necessary to the activity of the muscle, and in greater quantity in proportion to the increase of work; and even if severe labour can sometimes be performed on a non-nitrogenous diet, it is possible only for a short time, and at the expense of the nitrogenous constituents of other parts of the body.

Pettenkofer a. Voit (*Zeitschr. f. Biologie*, ii. 566; *Chem. Centr.* 1867, p. 779; *Jahresb.* 1867, p. 790) also regard the assumption that muscular power is developed by the combustion of the non-azotised constituents of food, and that the excretion of urea is merely a consequence of a constant consumption of the muscles, as incorrect, especially because this consumption does not increase during exercise. They regard it as more probable that the storing up of albumin in the body, and the condensation of oxygen thereby, forms a reservoir for the muscular power, which can be drawn upon at pleasure (perhaps by elimination of oxygen and formation of carbonic acid and water from fat). The accumulation of disposible or potential energy takes place therefore but slowly, and by no means in proportion to the quantity of the products of combustion which are formed in the course of 24 hours. Before the elimination of carbonic acid can be increased in proportion to a more abundant supply of food, a larger quantity of oxygen must also be taken up, and this increased faculty of absorbing oxygen is but slowly acquired by the organism. Hence persons who have been badly nourished may live on a generous diet for a considerable time before they recover their full normal muscular power; and to patients suffering from diabetes or leukhæmia (in whom the power of absorbing oxygen is defective), strong muscular exertion is impossible, in spite of the most abundant nutriment. See further the experiments of Pettenkofer a. Voit (*Ann. Ch. Pharm.* cxli. 295; *Sitzungsber. d. Bayerischen Akad. d. Wissensch.* 1867, 1; *Zeitschr. f. Chem.* [2] iii. 30; *Phil. Mag.* [4] xxxiv. 30; *Jahresb.* 1866, p. 723; 1867, p. 781).

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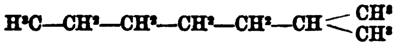
OBREGUIN. A substance intermediate in character between the fats and resins, occurring in Mexico on the twigs of *Alcea rosea.* It is nearly insoluble in alcohol, easily soluble in ether, chloroform, and turpentine oil, and remains, on evaporating its solutions, as a colourless inodorous mass, having the consistence of turpentine, and saponifiable by alkalis.

OCTANE. C^8H^{18}.—This hydrocarbon is one of the constituents of American petroleum. It is produced by the action of zinc and hydrochloric acid on secondary octyl iodide (Schorlemmer, *Proc. Roy. Soc.* xvi. 329); by that of sodium-amalgam on primary octyl iodide (Zincke, p. 878); and, together with others of the same series, by heating phthalic acid, $C^8H^6O^4$, indigo blue, C^8H^5NO, and acenaphthene, $C^{12}H^{10}$, with 80 pts. of saturated aqueous hydriodic acid (Berthelot, pp. 3, 728, 741); by the dry distillation of the lime-soap of Menhaden oil; and, according to Vohl (*Jahresb.* 1865, p. 841), by passing the vapour of tridecane, $C^{13}H^{28}$, through a red-hot iron tube.

The isomeric modifications of octane have not yet been very completely investigated. Schorlemmer (*Proc. Roy. Soc.* xvi. 370), from a comparison of the boiling point (124°) of octane obtained from secondary octyl alcohol with those of quintane (amyl hydride), C^5H^{12}, hexane (ethyl-butyl), C^6H^{14}, and heptane (ethyl-amyl), C^7H^{16}, infers that it has one of its carbon-atoms associated directly with three others—in other words, that it contains the radicle isopropyl—and is represented by the formula



$$H^3C—CH^2—CH^2—CH^2—CH^2—CH{<}\begin{matrix}CH^3\\CH^3\end{matrix}$$

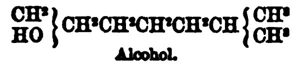
(see HYDROCARBONS, p. 709). From the experiments of Zincke (*Ann. Ch. Pharm.* clii. 15), it appears that octane prepared from primary octyl iodide has very nearly the same boiling point and specific gravity as that obtained from the secondary octyl iodide; and recent experiments by Schorlemmer (*ibid.* clii. 153) have shown that the octane from secondary octyl iodide and that obtained from petroleum yield, by conversion into octyl chloride and acetate, and saponification of the latter, both a primary and a secondary octyl alcohol: hence it seems probable that these hydrocarbons are themselves mixtures of two isomeric compounds; in fact, the octane from petroleum may be separated by long-continued fractional distillation into two hydrocarbons, C^8H^{18}, one boiling at 119°–122°, the other at 122°–125°.

OCTYL or **DIOCTYL,** $C^{16}H^{34}$, is produced, together with octane, when primary octyl iodide is heated with sodium-amalgam, and the product is subsequently rectified over sodium; it is easily separated from the octane by its higher boiling point, and may be purified by dissolving it in a small quantity of ether-alcohol, and cooling the solution by a freezing mixture, whereupon it solidifies to a crystalline pulp, which, after the liquid has been quickly filtered off in the cold, must be washed with well-cooled alcohol and repeatedly pressed. It then forms white laminæ having a strong nacreous lustre, soluble in hot absolute alcohol or in ether, and separating from either solution in well-defined crystals. Hot concentrated alcoholic solutions become turbid on cooling, yielding drops of oil which afterwards solidify. Octyl melts at 21° and boils constantly at 278° (Zincke).

OCTYL ALCOHOLS and **ETHERS.** *Primary Octyl Alcohol*, or *Heptylcarbinol*, $C^7H^{15}.CH^2OH$, and the corresponding *acetate*, $C^7H^{15}.CH^2OC^2H^3O$, are contained in the volatile oil obtained from the seeds of the cow-parsnep (*Heracleum Spondylium*). The comparatively small portion of this oil which boils between 190° and 195° consists mainly of the alcohol; but by far the greater portion passes over between 200° and 212°, and this by continued fractionation, yields primary octyl acetate, $C^{10}H^{20}O^2$; boiling between 206° and 208°. This compound is insoluble in water, easily soluble in alcohol and ether, and has a sp. gr. of 0·8717 at 16°. Heated with alcoholic potash, it yields potassium acetate, and an oil which floats on the surface and distils completely between 185° and 195°. To obtain the whole of it, the alkaline liquid is mixed with common salt, and the separated oil is washed therewith, then dried with fresh quick lime, and distilled.

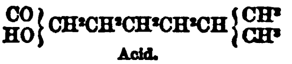
The colourless oily liquid thus obtained is primary octyl alcohol. It has a sp. gr. of 0·830 at 16°, boils between 190° and 192°, is nearly insoluble in water, miscible with alcohol and ethers, has a peculiar pungent aromatic odour, and tastes sweetish at first, afterwards burning and sharp (Zincke, *Ann. Ch. Pharm.* clii. 1).

By boiling for some hours with potassium dichromate and dilute sulphuric acid, this alcohol is converted into an acid, $C^8H^{16}O^2$, melting at 16° to 17°, and isomeric or identical with the caprylic acid of natural fats, together with the corresponding octylic ether, $C^8H^{17}.C^8H^{15}O^2$. This reaction shows it to be a primary alcohol; and from the boiling point of the octane derived from it (p. 897), it appears to be an iso-alcohol, that is to say, to contain the radicle isopropyl. The structural formulæ of the alcohol, and of the caprylic acid derived from it, are accordingly:



$$\left.\begin{matrix}CH^2\\HO\end{matrix}\right\}CH^2CH^2CH^2CH^2CH\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right.$$

Alcohol.



$$\left.\begin{matrix}CO\\HO\end{matrix}\right\}CH^2CH^2CH^2CH^2CH\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right.$$

Acid.

If the alcohol were a normal alcohol, the octane derived from it should boil, if Schorlemmer's views are correct, at 131·5°. (See HYDROCARBONS, p. 709.) The boiling points of the alcohol and its derivative are (like those of primary alcohols and ethers in general) considerably higher than those of the corresponding secondary octylic compounds derived from castor-oil alcohol (Zincke, *Ann. Ch. Pharm.* clii. 1).

Primary octyl alcohols are likewise obtained from octane by converting that hydrocarbon into octyl chloride, then into acetate, and saponifying the latter with alcoholic potash; secondary alcohols are however formed at the same time. The primary alcohol thus obtained from octane prepared from secondary octyl iodide, yields by oxidation with chromic acid mixture, an acid having the composition $C^8H^{16}O^2$, but differing both from the caprylic acid of natural fats, and from that obtained by oxidation of the octylic alcohol of Heracleum oil, inasmuch as when floating on water it remains liquid when cooled to 0°: hence the primary octyl alcohol from this variety of octane appears to be different from that of Heracleum oil. Octane from petroleum likewise yields a primary alcohol convertible by oxidation into an acid, $C^8H^{16}O^2$; but the quantity obtained was too small for the determination of its physical properties (Schorlemmer, *ibid.* clii. 152).

Primary Octyl Chloride, $C^8H^{17}Cl = C^7H^{15}.CH^2Cl$, is best prepared by saturating the alcohol from Heracleum oil at a low temperature with hydrochloric acid gas, heating for some time to 120°, and converting the small portion of the alcohol which then remains undecomposed, with phosphorus chloride. The *bromide* and *iodide* are obtained by treating the alcohol with bromine or iodine and red phosphorus. These three ethers are colourless liquids, insoluble in water, sparingly soluble in weak spirit, easily soluble in absolute alcohol and ether. Their boiling points and specific gravities are as follows:

	Boiling point	Sp. gr.
Chloride, $C^8H^{17}Cl$	179·5°–180·5°	0·8802 at 16°
Bromide, $C^8H^{17}Br$	198°–200°	1·1116 „
Iodide, $C^8H^{17}I$	220°–222°	1·1338 „

The primary octyl ethers of the fatty acids are colourless oily liquids, insoluble in water, soluble in alcohol and ether, and exhibiting an average difference of 15° in boiling point for each difference of CH^2:

		Boiling point	Sp. gr.
Acetate,	$C^8H^{17}.C^2H^3O^2$	206° to 208°	0·8717 at 16°
Valerate,	$C^8H^{17}.C^5H^9O^2$	249° „ 251°	0·8642 „
Caproate,	$C^8H^{17}.C^6H^{11}O^2$	268° „ 271°	—
Caprylate,	$C^8H^{17}.C^8H^{15}O^2$	297° „ 299°	0·8625 „

The acetate and caproate exist ready-formed in Heracleum oil; the caprylate was obtained by oxidising the alcohol with chromic acid; the valerate by heating the bromide in sealed tubes with potassium valerate (Zincke).

Secondary Octyl Alcohols.—The eight-carbon alcohol obtained from castor-oil (iv. 170) is converted by oxidation with chromic acid mixture into a ketone, namely methyl-œnanthol or methyl-hexyl ketone, $C\left\{\begin{array}{l}CH^3\\C^6H^{13}\\O\end{array}\right.$, which, by further oxidation, yields acetic and caproic acids: hence this alcohol consists of methyl-hexyl carbinol, $C\left\{\begin{array}{l}CH^3\\C^6H^{13}\\H\\OH\end{array}\right.$. Further, by converting it into the corresponding iodide, and treating this iodide with zinc and hydrochloric acid in a flask surrounded with cold water, octane, C^8H^{18}, is obtained as an oily liquid, which when freed from adhering traces of iodide and alcohol by treatment with nitric and sulphuric acids, boils at 124°. This hydrocarbon is inferred, from considerations already adduced, to contain the radicle isopropyl (p. 709), and accordingly the alcohol from which it is produced is regarded as constituted according to the formula $C\left\{\begin{array}{l}CH^3\\CH^2CH^2CH^2CH(CH^3)^2\\H\\OH\end{array}\right.$ (Schorlemmer, *Proc. Roy. Soc.* xvi. 376).

The same alcohol is obtained, together with a very small quantity of the primary alcohol, from the octane of American petroleum. This liquid treated with chlorine yields an octyl chloride, $C^8H^{17}Cl$, having an odour of oranges, and boiling at 173° to 176°; the latter heated to 200° with strong acetic acid and potassium acetate, is converted into octylene, together with a comparatively small quantity of octyl acetate, a liquid having an odour of pears and boiling at 200°–205°; and by heating this acetate with alcoholic potash-solution, treating the resulting liquid with water, washing the oily liquid thereby separated several times with water, and drying it over fused potash, an octyl alcohol is obtained boiling at 180°–182°, having exactly the same odour as the castor-oil alcohol, and yielding by oxidation (together with a little caprylic acid) the same products of oxidation as the latter.

Another secondary octyl alcohol is obtained, together with a larger proportion of the primary alcohol, by a similar series of operations on the octane produced by reduction of the secondary octyl iodide corresponding to castor-oil alcohol (p. 877). This octane yields a chloride having but a slight odour of oranges, boiling at 174°–176°, and likewise converted by heating with alcoholic potash into octylene and octyl acetate; but these two products are formed in about equal quantities, whereas the octyl chloride from petroleum octane yields about three times as much octylene as octyl acetate. The acetate thus obtained has also an odour of pears, and boils at 198°–202°. The alcohol prepared from it by heating with alcoholic potash boils between 180° and 190°, the greater portion between 182° and 186°. It smells very much like methyl-hexyl carbinol, and likewise yields, by oxidation with chromic acid mixture, an acid, $C^8H^{16}O^2$, isomeric with caprylic acid, and a ketone isomeric with methyl-œnanthol; but this ketone yields by further oxidation, propionic and valeric acids, without a trace of acetic: hence it consists of ethyl-caproyl or ethyl-amyl ketone, $C\left\{\begin{array}{l}C^2H^5\\C^5H^{11}\\O\end{array}\right.$, and the alcohol which yields it is ethyl-amyl carbinol, $C\left\{\begin{array}{l}C^2H^5\\C^5H^{11}\\H\\OH\end{array}\right.$ (Schorlemmer, *Ann. Ch. Pharm.* clii. 152).

A secondary octyl alcohol, perhaps different from both the preceding, is obtained from octylene (De Clermont, *Compt. rend.* lxvi. 1211; *Ann. Ch. Pharm.* cxlix. 38). This hydrocarbon heated in a sealed tube with saturated aqueous hydriodic acid is converted into *secondary octyl iodide*, or *octylene hydriodide*, $C^8H^{16}.HI$; the latter is decomposed at ordinary temperatures by silver acetate, yielding a secondary *octyl acetate* or *octylene monoacetate*, $C^8H^{16}.HC^2H^3O^2$, together with octylene and acetic acid; and the acetate distilled with finely pulverised potassium hydrate, yields the secondary octyl alcohol, which for distinction may be provisionally called octylene hydrate.

This alcohol, $C^8H^{18}O$ or $C^8H^{16}.H^2O$, is, after rectification, a colourless, mobile liquid, which does not stain paper, has an aromatic odour, and a burning persistent taste, is insoluble in water, but soluble in alcohol and ether; burns with a luminous flame. Boils at 174°–178° (lower than either of the preceding modifications); has a sp. gr. of 0·811 at 0° and 0·793 at 23°. It is not decomposed by heating to 280° for twenty hours. By oxidation with chromic acid mixture at the boiling heat it is converted, partly into methyl-œnanthol, partly by further oxidation into acetic and caproic acids. It yields, therefore, the same oxidation-products as octyl alcohol from castor-oil, and must therefore consist, like the latter, of methyl-hexyl carbinol; but its boiling point, and those of the corresponding ethers, so far as they have been examined, are lower than those of the castor-oil alcohol and its compound ethers: it is probable therefore that the hexyl radicles in the two alcohols are differently constituted (De Clermont, *Bull. Soc. Chim.* [2] xii. 212).

Octylene hydriodide, obtained by heating octylene or the alcohol with saturated hydriodic acid, has a sp. gr. of 1·314 at 21°, and boils at 120° (the iodide from castor-oil alcohol at 193° according to Squire, 210° according to Bouis). The *hydrobromide* boils at a lower temperature. The *acetate* has a sp. gr. of 0·822 at 0° and 0·803 at 26°, and boils at about 176° (that from the castor-oil alcohol at 193° Bouis).

Tertiary Octyl Alcohol or *Propyl-diethyl Carbinol*, $C\left\{\begin{matrix}C^3H^7\\C^2H^5\\C^2H^5\\OH\end{matrix}\right.$ is produced by treating butyryl chloride, C^3H^7COCl, with zinc-ethyl, leaving the product for several days till it becomes viscid, then heating it in the water-bath, acidulating with hydrochloric acid, and distilling. The tertiary alcohol then passes over, and after being freed from an admixed ketone by agitation with sodium bisulphite, may be purified by distillation over ignited potassium carbonate. Its formation is represented by the equations:

$$\underset{\text{Butyryl chloride.}}{C^3H^7COCl} + Zn(C^2H^5)^2 = ZnO + \underset{\text{Propyl-diethyl chloromethane.}}{C\left\{\begin{matrix}C^3H^7\\(C^2H^5)^2\\Cl\end{matrix}\right.}$$

$$\underset{\text{Propyl-diethyl chloromethane.}}{C\left\{\begin{matrix}C^3H^7\\(C^2H^5)^2\\Cl\end{matrix}\right.} + HOH = HCl + \underset{\text{Propyl-diethyl carbinol.}}{C\left\{\begin{matrix}C^3H^7\\(C^2H^5)^2\\OH\end{matrix}\right.}$$

This alcohol is similar in its properties to the tertiary butyl and hexyl alcohols (pp. 374, 698), being a somewhat viscid liquid, lighter than water, and slightly soluble therein; it has an alcoholic and camphorous odour and does not solidify in a freezing mixture. With phosphorus pentachloride it forms an octyl chloride, $C^8H^{17}Cl$, having a peculiar and unpleasant odour, and boiling at 155°. By oxidation with chromic acid mixture it yields propionic and acetic acids (Buttlerow, *Bull. Soc. Chim.* [2] v. 17).

OCTYLENE ACETOCHLORHYDRIN. $C^{10}H^{19}ClO^2 = C^8H^{16}\left\{\begin{matrix}OC^2H^3O\\Cl\end{matrix}\right.$.— This compound is produced by direct combination of octylene with aceto-hypochlorous anhydride or chlorine acetate, $ClC^2H^3O^2$, prepared by Schützenberger's method (p. 25). Hypochlorous anhydride prepared from dry chlorine and mercuric oxide is passed into 50 grams of acetic anhydride cooled to a low temperature, till an increase of weight amounting to 10 grams has been attained, whereby the liquid is one-fourth saturated; this limit must not be exceeded, for fear of explosion. The mixture is added by drops to 14 grams of pure octylene, previously diluted with acetic anhydride and glacial acetic acid, and cooled by a freezing mixture to moderate the action. Combination then takes place, attended with rise of temperature, and on subsequently adding water, the acetochlorhydrin separates, and may be purified by washing with water, drying over calcium chloride, and rectification. It is a light mobile liquid, having a pleasant aromatic odour and burning taste; soluble in alcohol, ether, and acetic acid, insoluble in water; burns with a bright green-edged flame. Boiling point 225°. Sp. gr. = 1·026 at 0°, 1·011 at 18°. Vapour-density obs. = 7·32; calc. = 7·12. It is not altered by cohobation for several days with caustic potash, but when heated to 180° in a sealed tube with potassium hydrate for forty hours, it is partially saponified, the product yielding by fractional distillation a liquid which boils at 145°, and has nearly the composition of octylene oxide, $C^8H^{16}O$ (De Clermont, *Compt. rend.* lxviii. 1323; *Zeitschr. f. Chem.* [2] v. 469).

ŒNANTHOL-UREAS. See Urea.

OILS and **FATS.** For the extraction of oils from seeds, H. Vohl (*Dingl. pol. J.* clxxxii. 319; *Jahresb.* 1866, p. 893) recommends the light hydrocarbons of Canadian petroleum boiling at about 60° (which he calls *Canadol*), instead of carbon bisulphide.

On the testing of fixed oils, see Donny, *Bull. Soc. d'Enc.* 1864, p. 372; *Dingl. pol. J.* clxxiv. 78; *Jahresb.* 1864, p. 734;—Dragendorff, *Russ. Zeitschr. Pharm.* ii. 434; *Jahresb.* 1864, p. 734;—Nicklès, *Bull. Soc. Chim.* [2] vi. 89; *Jahresb.* 1866, p. 827;—Jacobsen, *Bull. Soc. Chim.* [2] vii. 96; *Jahresb.* 1866, p. 827.

A method of determining the quantity of fatty oil in seeds, &c., by exhausting the substance with a volatile solvent, as ether, benzene, or carbon bisulphide, evaporating the solvent, and weighing the residual oil, is described by R. Hoffmann (*Zeitschr. anal. Chem.* vii. 368; *Zeitschr. f. Chem.* [2] iv. 530).

The amount of oil obtainable from various seeds, European and exotic, has been determined by Cloez (*Bull. Soc. Chim.* [2] iii. 41–50; *Jahresb.* 1865, p. 629), and by Münch (*N. Jahrb. Pharm.* xxv. 8; *Jahresb.* 1866, p. 698); from seeds of various Indian plants by J. Lepine (*J. Pharm.* [2] xl. 16; *Jahresb.* 1861, p. 741). The proportion of olein, stearin, and palmitin in the seeds of various Indian plants has been determined by Oudemanns (*J. pr. Chem.* xcix. 407; c. 409; *Bull. Soc. Chim.* [2] viii. 121; *Jahresb.* 1866, p. 696).

Mège-Mouriès (*Compt. rend.* lviii. 864; lx. 735; *Jahresb.* 1864, p. 809) describes a new method of saponification, founded on the property of fats in the state of emulsion (*état globulaire*) to take up soda-ley containing common salt. See also De Milly and Legrand, *Bull. Soc. d'Encouragement*, 1864, xi. 406, 410; *Dingl. pol. J.* clxxvi. 145, 151; *Jahresb.* 1865, p. 843;—F. Knapp, *Dingl. pol. J.* clxxx. 309; *Jahresb.* 1865, p. 844.

A detailed account of the methods in use for the manufacture of fatty acids, with an experimental examination of the various statements relating to the decomposition of fats by sulphuric acid, is given by J. Stas ('Auszug aus einem Bericht über die Londoner Industrie-Ausstellung von 1862,' aus *Schweizerische polytechn. Zeitschrift*, ix. 138, in *Dingl. pol. J.* clxxv. 68; *Jahresb.* 1865, p. 845).

On the saponification of fats by lime, see H. L. Buff (*Inauguraldissertation Göttingen*, 1863; abstr. *Dingl. pol. J.* clxxiii. 53; *Jahresb.* 1864, p. 808). The same author (*loc. cit.*) has given a report on the manufacture of fatty acids and glycerin, and a history of the investigations relating to the chemical nature of fats.

OKENITE. According to E. E. Schmid (*Pogg. Ann.* cxxvi. 148; *Jahresb.* 1865, p. 889), this mineral gives off two-thirds of its water at 100°, being thereby reduced to $3(CaO.2SiO^2) + 4H^2O$.

OLEIC ACID. $C^{18}H^{34}O^2$ (Overbeck, *J. pr. Chem.* xcvii. 159; *Zeitschr. f. Chem.* [2] i. 509; ii. 186; *Jahresb.* 1865, p. 326; 1866, p. 330).—When 1 mol. bromine is gradually added to cooled oleic acid, oleic dibromide (or dibromostearic acid), $C^{18}H^{34}Br^2O^2$, is produced, and may be purified by saponifying it with dilute potash-ley (containing not more than 1 mol. KHO to 1 mol. of the dibromide), dissolving the white soap-cake in dilute alcohol, decomposing it with hydrochloric acid, dissolving the washed oil in ether, and evaporating, finally over sulphuric acid. It then remains as a yellow syrupy oil, heavier than water, insoluble therein, easily soluble in alcohol and ether, and not decomposing till heated above 100°. Its salts are viscid, unctuous, or gummy masses. When crude oleic acid which had been altered by exposure to the air was treated with bromine, a buttery product was obtained, the solution of which in a small quantity of alcohol deposited granular crystals having nearly the composition $C^{18}H^{33}Br^3O^2$ (iv. 194).

Monobromoleic acid, $C^{18}H^{33}BrO^2$, is produced by mixing the dibromide with at least 2 mol. potassium hydrate in alcoholic solution. The solution decanted from potassium bromide, and considerably diluted with water, deposits a light yellow oil, which when left to itself in a vacuum, yields white crystals melting at 35° to 36°, and probably consisting of monobromoleic acid containing a small quantity of stearolic acid. It is reduced to oleic acid by sodium-amalgam. *Monobromoleic dibromide* or *tribromostearic acid*, $C^{18}H^{33}Br^3O^2$, is formed by direct union of bromoleic acid with bromine, as a limpid viscid oil, easily soluble in alcohol and ether. Alcoholic potash removes part of the bromine at ordinary temperatures, and the whole when heated, forming stearolic acid.

Elaïdic dibromide (Burg's dibromelaïdic acid) is likewise converted into stearolic acid by heating with alcoholic potash to 180°.

OLEOPHOSPHORIC ACID. See LECITHINE (p. 779).

OLIVIN. On the occurrence of this mineral in trap-rocks and other formations, see Tschermak (*Wien. Akad. Ber.* lii. [1] 265; lvi. [1] 261; *Jahresb.* 1865, p. 923; 1867, p. 1025). On olivin in meteorites: Daubrée (*Compt. rend.* lxii. 200, 369, 666; *Jahresb.* 1866, p. 1002). On olivin-rock: Sandberger (*Jahrb. Min.* 1866, p. 385; *Jahresb.* 1866, p. 978) and Kjerulf (*Jahrb. Min.* 1867, p. 480; *Jahresb.* 1867, p. 1025).

OPIANIC ACID, $C^{10}H^{10}O^5$, is formed, together with other products, by boiling an alcoholic solution of narcotine-tri-iodide (*Jörgensen*, p. 865).

Opianic acid heated with concentrated hydrochloric or hydriodic acid, is converted, with evolution of methyl chloride or iodide, into methyl-noropianic acid, $C^9H^8O^5$, a compound intermediate between normal opianic acid (see NARCOTINE) and opianic (dimethyl-noropianic) acid:

$$\underset{\substack{\text{Normal}\\ \text{opianic}\\ \text{acid.}}}{C^8H^6O^5} \qquad \underset{\substack{\text{Methyl-}\\ \text{noropianic}\\ \text{acid.}}}{C^9H^8O^5} \qquad \underset{\substack{\text{Opianic}\\ \text{(dimethyl-noropianic)}\\ \text{acid.}}}{C^{10}H^{10}O^5}$$

Methyl-noropianic acid is monobasic. It dissolves in cold, but more easily in boiling water, and crystallises therefrom with 2½ mol. water. Like hypogallic acid, it forms with ferric chloride a dark blue liquid, which, however, on addition of ammonia, becomes, not blood-red, but light red. By dilute nitric acid it is converted into *nitromethyl-noropianic acid*, $C^9H^7(NO^2)O^5$, which crystallises with 1 mol. water (Matthiessen a. Foster, *Chem. Soc. J.* [2] vi. 357).

OPINIC and ISOPINIC ACIDS. $C^{14}H^{10}O^8$.—Isomeric acids produced, according to Liechti (*Zeitschr. f. Chem.* [2] vi. 196), by the action of hydriodic acid upon hemipinic acid:

$$\underset{\substack{\text{Hemipinic}\\ \text{acid.}}}{2C^{10}H^{10}O^6} + 4HI = \underset{\substack{\text{Methyl}\\ \text{iodide.}}}{4CH^3I} + \underset{\substack{\text{Oxalic}\\ \text{acid.}}}{C^2H^2O^4} + \underset{\substack{\text{Opinic}\\ \text{acid.}}}{C^{14}H^{10}O^8}$$

The oxalic acid is resolved by the further action of the hydriodic acid into water and the oxides of carbon. The two isomeric acids crystallise from the solution, and are easily separated by recrystallisation. *Opinic acid* crystallises in prisms or tables containing $C^{14}H^{10}O^8.3H^2O$, which gradually turn yellow on exposure to the air; it gives off its water at 100°, is converted at 105° into a viscid tenacious mass, melts and partly sublimes at 148°; when heated on platinum foil it gives off an odour of vanilla. It dissolves easily in water and alcohol, very slightly in ether; colours ferric chloride bluish-violet; reduces ammoniacal silver solution slowly, Fehling's copper solution not at all even when heated.

Isopinic acid crystallises in nodules, also containing 3 mol. water, more soluble in water than opinic acid, easily soluble in alcohol, sparingly in ether. It gives off ⅔ of its water of crystallisation over oil of vitriol, the rest at 100°; sublimes at 130°, begins to melt at 144°, melts completely at 148°, and emits an odour of vanilla when more strongly heated. In its original state it forms a blue solution with ferric chloride, but after fusion a green solution. It is a more powerful reducing agent than opinic acid, decomposing Fehling's solution when heated.

Liechti regards isopinic acid as identical with Matthiessen and Foster's hypogallic acid (iii. 239), which, according to his view, is not isomeric with oxysalicylic acid.

OPIUM-BASES. Cl. Bernard (*Arch. Pharm.* [2] cxix. 240) divides the opium-bases, according to their observed action upon animals, into the three following classes, in each of which the most active base is placed first:

Narcotic.	*Exciting.*	*Poisonous.*
Narceine.	Thebaine.	Thebaine.
Morphine.	Papaverine.	Codeine.
Codeine.	Narcotine.	Papaverine.
	Codeine.	Narceine.
	Morphine.	Morphine.
	Narceine.	Narcotine.

On the physiological action of the opium-bases, see also Baxt (*Wien. Akad. Ber.* lvi. [2] 189; *Jahresb.* 1867, p. 525). For their solubilities and reactions, see ALKALOIDS (p. 87).

Several new bases have lately been obtained by Hesse (*Ann. Ch. Pharm.* cliii. 47) from the aqueous extract of opium—namely, *codamine*, $C^{19}H^{23}NO^3$, *lanthopine*, $C^{23}H^{25}NO^4$, *laudanine*, $C^{20}H^{25}NO^3$, and *meconidine*, $C^{21}H^{23}NO^4$. To separate them, the aqueous extract is precipitated with excess of lime or sodium carbonate; the liquid separated from the precipitate is agitated with ether; and the ethereal extract is mixed with acetic acid. After removing the ether, the acid solution is poured in a thin stream into moderately dilute potash- or soda-ley, the alkali being kept in excess, and the liquid stirred to prevent the caking together of a resinous precipitate (P) containing papaverine and thebaine. This precipitate is separated after 24 hours, and the filtrate, after supersaturation with hydrochloric acid, is immediately mixed with ammonia, whereby a flocculent precipitate is formed, then with chloroform without previous filtration, and the chloroform solution is treated with acetic acid. After removal of the chloroform, the acid solution is exactly neutralised with ammonia, whereby a reddish, resinous, quickly crystallising precipitate is formed, containing lanthopine. After 24 hours the yellowish solution is decanted, filtered, and added to the small quantity of potash-ley sufficient to precipitate it (this quantity must, however, be large enough to decompose all the acetate of ammonia in the liquid, and leave an excess sufficient to precipitate the bases). The potash-solution thus obtained is turbid from separated codeine, which may be completely removed by agitating the liquid with ether, as it is much more soluble in ether than the other bases; the latter, indeed, are not taken up by the ether till they have been set free by sal-ammoniac. The ethereal solution left to evaporate very slowly in a tall narrow cylinder yields in the first place a crystallisation of laudanine; and on diluting the mother-liquor with a little ether, washing with bicarbonate of soda, and leaving the ether to evaporate, crystals of codamine are very soon deposited. The mother-liquor contains meconidine, together with another base, *x*, not yet examined.

These bases and their salts are described in their alphabetical places. The quantities of them contained in opium are extremely small. A sample of Turkey opium containing 8·3 p. c. morphine yielded only 0·0058 p. c. lanthopine, 0·0052 p. c. laudanine, and 0·0033 p. c. codamine.

Codamine and laudanine form a homologous series with morphine and codeine:

$C^{17}H^{19}NO^3$	$C^{18}H^{21}NO^3$	$C^{19}H^{23}NO^3$	$C^{20}H^{25}NO^3$
Morphine.	Codeine.	Codamine.	Laudanine.

Pseudomorphine, $C^{17}H^{19}NO^4$ (iii. 1051), and apomorphine, $C^{17}H^{17}NO^2$ (p. 839), are lateral members of this series.

A second group of homologous opium-bases includes papaverine, $C^{21}H^{21}NO^4$, and lanthopine, $C^{23}H^{25}NO^4$, to which are related cryptopine, $C^{23}H^{25}NO^5$, and the isomeric bases rhœadine and rhœagenine, $C^{21}H^{21}NO^6$. Rhœagenine, the salts of which resemble those of papaverine in many respects, may indeed be regarded as dioxypapaverine, and cryptopine as oxylanthopine. Meconidine, $C^{21}H^{23}NO^4$, contains 2 at. hydrogen more than papaverine, and is homologous with sanguinarine or chelerythrine, $C^{19}H^{17}NO^4$ (v. 188), the alkaloïd contained in the common celandine, also a papaveraceous plant (Hesse).

OPOPONAX. This resin fused with potassium hydrate is converted into protocatechuic acid, a small quantity of pyrocatechin, and an acid precipitated by lead acetate, but not yet analysed (Hlasiwetz a. Barth, *Jahresb.* 1866, p. 630).

OPOSIN. An albuminous substance obtained, together with syntonin, from muscular flesh. It is found in the expressed flesh-juice, and appears to exist more abundantly in mutton than in beef. The solution of well-washed syntonin in water containing hydrochloric acid is not precipitated by mercuric chloride; but that of oposin gives a precipitate both with mercuric chloride and with strong hydrochloric acid. The platinum salts of both these bodies contain from 10 to 11 p. c. platinum (Commaille, *J. Pharm.* [4] iv. 108).

ORANGE-TREE. T. E. Thorpe (*Chem. Soc. J.* [2] vi. 515) has analysed the ash of the root, stem, branches, and fruit of a diseased orange-tree from the Balearic Isles, where the orange-trees have lately suffered from a very formidable malady. The ash of all parts of the diseased tree was found to differ considerably from that of the corresponding parts of a healthy orange-tree, exhibiting especially an increased proportion of lime, and a diminished proportion of phosphoric acid, excepting in the fruit, in which there was a large excess of potash. It is not known whether these deviations have any connection with the origin of the disease, or whether they are merely consequences of it.

ORCHELLA WEED. Two varieties of orchella weed are used for the preparation of archil or orchil, namely *Rochella tinctoria*, imported from the Cape de Verde islands and from Chile, and *Rochella fuciformis*, imported from Angola, Zanzibar, Madagascar, and Lima. The former treated with milk of lime yields lecanoric acid (with which Stenhouse's α and β orsellic acids have been shown to be identical, both by himself and by Gerhardt); the latter was found by Hesse to yield erythric acid (Stenhouse, *Chem. Soc. J.* [2] v. 221).

For estimating the amount of colouring matter in these and other lichens, Stenhouse formerly gave the two following methods: (1) The lichen is exhausted with milk of lime; the clear liquor is precipitated with acetic acid; and the precipitated colouring matter is collected on a weighed filter, dried at the ordinary temperature, and weighed. —(2) The comminuted lichen (100 grains) having been macerated with milk of lime till all the colouring matter is extracted, a titrated solution of calcium hypochlorite is gradually added to the clear filtrate, whereby a blood-red colour is at first produced, which shortly disappears, leaving the liquid of a deep yellow colour. The addition of the hypochlorite must be continued, at last by drops, as long as these changes of colour continue to be produced. The number of measures of the hypochlorite solution required to destroy the colouring matter determines the amount of it in the solution (*Phil. Trans.* 1848). Stenhouse now modifies this last process by exhausting the lichen with weak caustic soda, and using a standard solution of sodium hypochlorite instead of the corresponding calcium salt. The advantage of this modification of the method is that the liquor remains quite transparent during the entire process (*Chem. Soc. J.* [2] v. 226).

ORCIN. $C^7H^8O^2 = C^7H^6(H^2O^2)$.—This substance appears to have the constitution of a diatomic phenol, inasmuch as it is produced by abstraction of CO^2 from orsellinic acid, $C^8H^8O^4$ (by boiling it with baryta-water), just as oxyphenol or pyrocatechin, $C^6H^6O^2$, is produced from oxysalicylic acid, $C^7H^6O^4$.

Respecting the preparation of orcin (and erythrite) from erythrin, see ERYTHRITE (p. 582). The nearly colourless solution of orcin in benzol is agitated in a glass flask with about one-tenth of its bulk of water, which extracts the orcin from the benzol. The aqueous solution thus obtained generally deposits crystals of orcin on cooling, and the whole of the orcin may be separated by sufficient concentration. It may be obtained colourless by a second treatment with benzol and recrystallisation from water (Stenhouse, *Chem. Soc. J.* [2] v. 223).

Orcin heated for some time above its boiling point remains liquid several hours after cooling, and at last solidifies suddenly, with evolution of heat. Vapour-density obs. = 4·20; calc. = 4·28. Orcin dissolves without alteration in caustic potash; does not oxidise in contact with platinum-black; is not attacked by concentrated hydriodic acid; when fused with phosphorus iodide it gives off hydriodic acid, and forms a resin soluble in alkalis. Aqueous orcin dissolves the hydrates of barium and calcium in considerable quantity, the solutions, when heated or mixed with alcohol, yielding precipitates of indefinite composition which turn red on exposure to the air (De Luynes, *Ann. Ch. Phys.* [4] vi. 184; *Jahresb.* 1865, p. 591). In contact with sulphur chloride, orcin is converted, with evolution of hydrochloric acid, into a sulphur-yellow amorphous compound, insoluble in water, alcohol, benzol, and carbon bisulphide, but dissolving with partial decomposition in alkalis (Stenhouse).

Anhydrous orcin heated in ammonia gas melts and absorbs a considerable quantity. A solution of orcin in 3 or 4 pts. ether saturated with ammonia, deposits on standing large octohedral crystals of orcin-ammonia, $C^7H^8O^2.NH^3$. This compound when quickly dried in a vacuum is colourless and inodorous, easily soluble in alcohol, sparingly in ether; it is not altered by dry oxygen, even when exposed to it for months, but on adding a little water it takes up oxygen and becomes coloured in a few hours; on exposure to the air it takes up water, gives off ammonia, and turns violet. It is likewise oxidised and coloured by permanganate of potassium, chromate of potassium or ammonium, and peroxide of barium, these compounds being reduced, and the products forming lakes with the colouring matter. It also reduces arsenic acid and ammoniacal solution of cupric sulphate. When orcin is heated to 45°–50° with aqueous ammonia, the surface of the liquid being constantly renewed and the ammonia replaced as it evaporates, the solution in about a week becomes viscid and violet coloured, and when filtered yields a violet liquid, which leaves on evaporation a violet resinous mass resembling orcin, and a brown precipitate, the alcoholic solution of which deposits colourless crystals covered with a brown powder (De Luynes, *loc. cit.*; also *Zeitschr. f. Chem.* [2] iv. 700).

Orcin unites directly with *picric acid*, forming the compound $C^7H^8O^2.C^6H^3(NO^2)^3O$, the aqueous solution of which dyes silk yellow, like free picric acid. With *pyrogallic acid* it forms a compound which crystallises in large laminæ, and blackens slightly on exposure to the air. Aqueous solutions of orcin and *nicotine* when mixed deposit a compound of the two in oily drops, which dissolve in excess of nicotine. An aqueous solution of orcin dissolves *rosaniline*, with deep red colour. Orcin deliquesces in gaseous *ethylene oxide*, 1 gram of it absorbing more than 400 c. c. of the gas, which it does not give up again in contact with solid potash. On adding *common salt* in excess to an aqueous solution of orcin, the two combine and form a crystalline precipitate, which fills the entire liquid (De Luynes, *Zeitschr. f. Chem.* [2] iv. 703).

Diacetyl-orcin, $C^{11}H^{12}O^4 = C^7H(C^2H^3O)^2O^2$, is formed by the action of acetyl chloride on pulverised orcin, and remains, on evaporating its ethereal solution, as an oily body, which crystallises in needles when cooled below 25°. It melts at 25°, then remains liquid for a long time even if cooled to 0°, and solidifies suddenly by contact with a crystal. It is nearly insoluble in water, very soluble in alcohol and ether, makes a transient greasy stain on paper, evaporates when heated, leaving a small quantity of charcoal, and is resolved by boiling with alkalis into orcin and acetic acid. It acquires a transient red colour in contact with chloride of lime, and is converted in an atmosphere of ammonia into ammonium acetate and orceïn. *Dibutyryl orcin*, $C^7H^6(C^4H^7O)^2O^2$, formed by the action of butyryl chloride on fused orcin, is a colourless uncrystallisable liquid, which reacts like the acetyl compound. *Dibenzoyl orcin*, $C^7H^6(C^7H^5O)^2O^2$, crystallises in hard colourless needles, inodorous, but having a sweet taste; melts at 40°, decomposes at a higher temperature, is insoluble in water, but dissolves easily in alcohol and ether, and is decomposed, by boiling with alkalis, into orcin and benzoic acid (De Luynes).

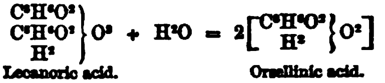
Alcoholic Orcins.—Methyl-orcin, $C^7H^7(CH^3)O^2$, *ethyl-orcin*, $C^7H^7(C^2H^5)O^2$, and *amyl-orcin*, $C^7H^7(C^5H^{11})O^2$, are produced by heating the corresponding alcoholic iodides with orcin in equivalent proportions. The first two are syrupy liquids; amyl-orcin crystallises in needles. *Diethyl-orcin*, $C^7H^6(C^2H^5)^2O^2$, and diamyl-orcin, $C^7H^6(C^5H^{11})^2O^2$, are formed by heating 1 mol. orcin with 2 mol. of the alcoholic iodide and potash. Both are syrupy; the ethyl-compound distils without decomposition between 240° and 250°. Lastly, when a large excess of the alcoholic iodide is used, together with potash, the compounds $C^7H^5(CH^3)^3O^2$, $C^7H^5(C^2H^5)^3O^2$, and $C^7H^5(C^5H^{11})^3O^2$ are produced. *Trimethyl-orcin* is liquid, and boils without decomposition at about 250° under ordinary pressure; *triethyl-orcin* at 265°. It has not yet been found possible to reconvert either of these compounds into orcin and the original alcohol. Diacetyl-orcin treated with sodium ethylate forms, together with sodium hydrate and ethyl acetate, a body soluble in water, but apparently not consisting of orcin (De Luynes a. Lionet, *Compt. rend.* lxv. 213).

Trinitro-orcinic acid, $C^7H^5(NO^2)^3O^2$, is produced by gradually adding orcin to strong nitric acid cooled by a freezing mixture, and dropping the resulting brown solution into strong sulphuric acid also cooled to a low temperature. On pouring the yellow pasty mixture thus produced into a considerable quantity of cold water, the trinitro-orcinic acid separates as a bright yellow crystalline powder, which may be purified by one or two crystallisations from boiling water. It then forms large yellow needles, soluble in alcohol, slightly soluble in cold water, readily in hot water. It is a strong acid, much resembling picric acid, but differs from the latter by the solubility of its salts. The *potassium salt*, $C^7H^3(NO^2)^3O^2K^2$, prepared by dissolving the acid in a warm and rather strong solution of potassium carbonate, solidifies on cooling to a mass of fine needles of a deep orange colour. The *sodium*, *calcium*, and *silver salts* crystallise well, and are moderately soluble in water; the *lead salt* is much less soluble.

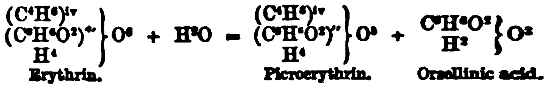
Beta-orcin, $C^8H^{10}O^2$, treated with nitric and sulphuric acids as above, yields a yellow substance which appears to be the corresponding nitro-compound of beta-orcin. Resorcin yields *trinitroresorcinic acid*, $C^6H^3(NO^2)^3O^2$, which crystallises readily, is of a much paler colour than trinitro-orcinic acid, but resembles it closely in most respects, and likewise forms crystalline salts (Stenhouse, *Chem. News*, xxii. 98; Aug. 26, 1870).

ORNITHITE. Tricalcic phosphate, $(PO^4)^2Ca^3 + 2H^2O$, found in monoclinic crystals in Sombrero guano (Julien, *Sill. Am. J.* [2] xl. 367).

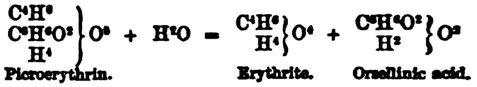
ORSELLINIC ACID. $C^8H^8O^4$.—Menschutkin (*Bull. Soc. Chim.* [2] ii. 424) regards this acid as diatomic, and represents its formation from lecanoric acid, erythrin, and picro-erythrin, by the following equations:



$$\underset{\text{Lecanoric acid.}}{\left.\begin{matrix}C^8H^6O^2\\C^8H^6O^2\\H^2\end{matrix}\right\}O^3} + H^2O = 2\left[\underset{\text{Orsellinic acid.}}{\left.\begin{matrix}C^8H^6O^2\\H^2\end{matrix}\right\}O^2}\right]$$

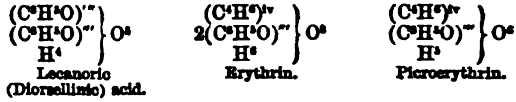


$$\underset{\text{Erythrin.}}{\left.\begin{matrix}(C^4H^6)^{iv}\\(C^8H^6O^2)^{iv}\\H^4\end{matrix}\right\}O^8} + H^2O = \underset{\text{Picroerythrin.}}{\left.\begin{matrix}(C^4H^6)^{iv}\\(C^8H^6O^2)''\\H^4\end{matrix}\right\}O^6} + \underset{\text{Orsellinic acid.}}{\left.\begin{matrix}C^8H^6O^2\\H^2\end{matrix}\right\}O^2}$$



$$\underset{\text{Picroerythrin.}}{\left.\begin{matrix}C^4H^6\\C^8H^6O^2\\H^4\end{matrix}\right\}O^6} + H^2O = \underset{\text{Erythrite.}}{\left.\begin{matrix}C^4H^6\\H^4\end{matrix}\right\}O^4} + \underset{\text{Orsellinic acid.}}{\left.\begin{matrix}C^8H^6O^2\\H^2\end{matrix}\right\}O^2}$$

Grimaux, on the other hand (*ibid.* iii. 410), regards orsellinic acid as monobasic, but triatomic, as represented by the formula $\left.\begin{matrix}(C^8H^5O)'''\\H^3\end{matrix}\right\}O^3$ (inasmuch as it is converted by loss of CO^2 into diatomic orcin), and alters Menschutkin's formula of the lichen-constituents as follows:



$$\underset{\substack{\text{Lecanoric}\\\text{(Diorsellinic) acid.}}}{\left.\begin{matrix}(C^8H^5O)'''\\(C^8H^5O)'''\\H^4\end{matrix}\right\}O^6} \qquad \underset{\text{Erythrin.}}{\left.\begin{matrix}(C^4H^6)^{iv}\\2(C^8H^5O)'''\\H^6\end{matrix}\right\}O^8} \qquad \underset{\text{Picroerythrin.}}{\left.\begin{matrix}(C^4H^6)^{iv}\\(C^8H^5O)'''\\H^3\end{matrix}\right\}O^6}$$

Ethyl Orsellinate, $C^8H^7O^4.C^2H^5$, is most conveniently prepared by digesting erythrin with 8 pts. absolute alcohol, distilling, boiling the viscid residue (consisting of ethyl orsellinate, picro-erythrin, and resin) with water, and the portion which crystallises from the aqueous solution with benzol, which dissolves the ethyl orsellinate and deposits it in crystals. *Ethyl di-iodorsellinate*, $C^8H^5I^2O^4.C^2H^5$, is formed by mixing a cold-saturated aqueous solution of ethyl orsellinate with a very dilute solution of iodine chloride containing excess of iodine, in quantity not sufficient for complete precipitation. The precipitate, washed with cold water and several times recrystallised from carbon bisulphide and alcohol, forms small needles soluble in benzol, carbon bisulphide, and hot alcohol, slightly soluble in boiling water. Heated above 100°, they melt and decompose, with liberation of iodine. *Methyl di-iodorsellinate*, $C^8H^5I^2O^4.CH^3$, prepared in a similar manner, likewise crystallises in needles (Stenhouse, *Chem. Soc. J.* [2] v. 224).

ORTHOCARBONATES. See Carbonates (i. 778; iv. 238).

ORTHOFORMATES. See Formates (p. 622).

OSMIUM. Experiments by Wöhler (*Ann. Ch. Pharm. Suppl.* iv. 253) seem to shew that the black oxide produced by fusing metallic osmium with potash is neither the trioxide, nor, as commonly supposed, the tetroxide (iv. 246), but an intermediate oxide, inasmuch as it dissolves in water with deep reddish-yellow colour (without perceptible evolution of gas), and is resolved by addition of acids into a black oxide and the tetroxide OsO^4. Such a solution concentrated to one-fourth, and left to cool out of contact with the air, deposits crystallised violet potassium osmite. On passing carbon dioxide through the yellow liquid decanted from the crystals, it first becomes colourless, then violet, with liberation of osmium tetroxide, and deposition of a greyish-violet precipitate. On treating this precipitate with water, a small quantity of brown oxide is separated, and a violet solution formed, from which nitric acid again precipitates black oxide, with formation of osmic acid. The solution of the violet crystals reacts with carbon dioxide in the same manner.

When sublimed osmium tetroxide is dissolved in excess of potash, and the deep yellow-red liquid is evaporated over potassium hydrate, opaque nodular groups of crystals are formed, soluble in water with reddish-yellow colour (without a trace of potassium osmite), and nitric acid added to the concentrated solution throws down, first white tetroxide, and then black oxide. The black oxide forms with concentrated hydrochloric acid, first a purple solution, which afterwards becomes yellow-brown, green, and when heated brownish-yellow, and is coloured pure yellow by sulphurous acid, without separation of metal, even at the boiling heat. Zinc precipitates osmium from this solution in black flocks.

OSTEOLITE. In osteolite from Eichen in the Wetterau, Church (*Chem. News*, xvi. 150) found 87·25 p. c. $(PO^4)^2Ca^3$, 5·70 CO^3Ca, 4·92 CaF^2, and 2·34 water: hence he concludes that it consists of apatite, more or less altered.

OXALIC ACID. $C^2H^2O^4$ =
$\begin{array}{l}COOH\\ |\\ COOH\end{array}$.—This acid is formed by reduction of carbonic acid. When dry carbon dioxide is passed into a flask containing metallic sodium and fine sand, and heated to about the boiling point of mercury, the mixture of sand and sodium being well stirred, sodium oxalate is produced by direct combination: $Na^2 + 2CO^2 = C^2O^4Na^2$. This product, spread out upon a plate to oxidise the remaining sodium, and then digested with water, yields a solution which, after neutralisation with acetic acid, forms with calcium chloride the characteristic precipitate of calcium oxalate (Drechsel, *Zeitschr. f. Chem.* [2] iv. 120). Oxalic acid is also formed by oxidising acetic acid in alkaline solution with potassium permanganate; $C^2H^4O^2 + O^3 = C^2H^2O^4 + H^2O$ (Lossen, *Ann. Ch. Pharm.* cxlviii. 174).

On the occurrence of oxalates in urine and urinary sediments, see Neubauer (*Zeitschr. f. Chem.* [2] v. 30).

By *potassium permanganate*, in acid solution, and likewise, though slowly, in alkaline solution, oxalic acid is oxidised to water and carbon dioxide (Berthelot). Harcourt (*Chem. Soc. J.* [2] v. 460) gives for this reaction in acid solution the equation:

$$K^2Mn^2O^8 + 3H^2SO^4 + 5H^2C^2O^4 = K^2SO^4 + 2MnSO^4 + 10CO^2 + 8H^2O.$$

The oxidation of oxalic to carbonic acid takes place quickly at the positive pole of a voltaic circuit. A neutral solution of potassium oxalate gives off at the positive pole, first carbon dioxide, then oxygen; an alkaline solution, first oxygen, then carbon dioxide (Burgoin, *Ann. Ch. Phys.* [4] xiv. 157).

Oxalic acid heated with concentrated aqueous *hydriodic acid* is resolved into carbon dioxide, carbon monoxide, and water (Berthelot).

The crystalline forms of several metallic oxalates have been examined by J. Loschmidt (*Wien. Akad. Ber.* li. [2] 7, 384; *Jahresb.* 1865, p. 374).

Calcium oxalate may be obtained in fine crystals by placing a layer of aqueous oxalic acid above a denser solution of sugar-lime (E. Monier, *Compt. rend.* lxiii. 1013). Both *calcium oxalate* and *lead oxalate* dissolve in the saccharine juice of beet (Scheibler, *Zeitschr. f. Chem.* [2] i. 62).

Manganous oxalate precipitated by adding a cold concentrated aqueous solution of oxalic acid to manganous sulphate, or ammonium oxalate to excess of manganous sulphate, has the composition $C^2O^4Mn + 3H^2O$; in the latter case the precipitation of the oxalic acid is complete (How, *Chem. News*, xix. 41).

Silver oxalate is commonly said to retain 2 p. c. water with great obstinacy (*Gmelin's Handbook*, ix. 169). According to Thudichum a. Wanklyn, however, this is not the case, the salt dried in a vacuum over sulphuric acid, and finally at 110°, being quite anhydrous (*Chem. Soc. J.* [2] vii. 294).

An *oxalato-chloride of strontium*, $C^2SrO^4.SrCl + 6H^2O$, is obtained in rhombic crystals by prolonged contact of a perfectly saturated solution of strontium chloride with washed and still moist strontium oxalate. It gives off 4 mol. water at 100°, is not altered by alcohol, but is resolved by water into its constituent salts. When the crystals of this salt are covered with two or three times their weight of a saturated solution of strontium chloride, and a solution of the same salt diluted with an equal bulk of water is gradually added at intervals of two or three hours, the rhombic crystals disappear, and are succeeded by prismatic crystals of the salt $3C^2SrO^4.SrCl^2 + 16H^2O$. This latter salt is also formed when the rhombic crystals are left for some time in an atmosphere saturated with aqueous vapour. In a similar manner may be obtained the double calcium salt, $C^2CaO^4.CaCl^2 + 7H^2O$, described by Fritzsche (iv. 255), and corresponding oxalato-chlorides of barium and magnesium (G. Rainey, *Proc. Roy. Soc.* xiv. 144).

Neutral thallium oxalate, $C^2Tl^2O^4 + 4H^2O$, forms short prismatic crystals. An acid salt, $C^4H^3TlO^8 + 2H^2O$, crystallises in large laminæ from a solution mixed with a considerable excess of oxalic acid (Carstanjen, *Jahresb.* 1867, p. 281).

Ethyl oxalate heated with sodium ethylate is converted into ethyl carbonate, with evolution of carbon monoxide, and simultaneous formation of sodium oxalate, a small quantity of sodium formate, and the sodium salts of complex organic acids (Löwig's 'nigric acids') (Geuther, *Zeitschr. f. Chem.* [2] iv. 656. Cranston a. Dittmar, *Chem. Soc. J.* [2] vii. 441). In the production of ethylic carbonate from ethylic oxalate, by the action of sodium (iv. 270), sodium ethylate appears to be formed in the first instance, which then reacts as above (Geuther).

OXALO-HYDROXAMIC ACID. $C^2H^4N^2O^4$.—An acid produced by the action of hydroxylamine on ethyl oxalate. (See HYDROXYLAMINE, p. 724.)

Meconidine is easily decomposed by strong *acids*, especially if heated. Its solution in dilute sulphuric acid becomes rose-coloured in a few minutes, purple-red in a few hours; at the boiling heat these changes of colour take place immediately. With acetic acid the change is much slower. Ammonia produces in the purple-red solution a dirty-white, very changeable precipitate. Strong sulphuric acid dissolves meconidine with olive-green colour; strong nitric acid colours it orange-red.

The *salts* of meconidine are very unstable. Their dilute solutions have an intensely bitter taste. From the acetic acid solution the meconidine is precipitated by *potash* or *soda* in white flocks, but is redissolved by excess of the reagent, and may be separated from the alkaline solution, after addition of sal-ammoniac, by ether, chloroform, and other solvents; acids precipitate it from the alkaline solution, but redissolve it when added in excess. *Ammonia* likewise precipitates the base, redissolves it when added in very large excess, but gives it up to ether or chloroform when agitated therewith. *Lime* reacts in a similar manner. The reaction with potash distinguishes meconidine from rhœadine, the salts of which give with potash a permanent crystalline precipitate.

Platinochloride of meconidine, $2(C^{21}H^{23}NO^4).PtCl^4$, is a yellow amorphous precipitate, which soon turns reddish. The *aurochloride* is a dingy yellow amorphous precipitate; the *mercurochloride* is a white amorphous precipitate, which in contact with hydrochloric acid soon acquires a rose colour.

MELACONITE. Native cupric oxide found at Copper Harbour, Lake Superior, in monoclinic crystals (Maskelyne, *Br. Assoc. Reports*, 35; *Notices and Abstracts*, 33; *Jahresb.* 1867, p. 979).

MELAMINE. $C^3H^6N^6$.—Syn. with CYANURAMIDE (ii. 287).

Triethyl-melamine, $C^3H^3(C^2H^5)^3N^6$, is produced by desulphuration of ethyl-sulphocarbamide. (See SULPHOCARBAMIDES.) By prolonged contact with cold hydrochloric acid, or by boiling for a short time with the same acid, it is converted into ammonia and triethyl-ammelide:

$$C^3H^3(C^2H^5)^3N^6 + H^2O = NH^3 + C^3H^2(C^2H^5)^3N^5O.$$

The platinochloride of triethyl-ammelide, $2[C^3H^2(C^2H^5)^3N^5O.HCl].PtCl^4$, crystallises in beautiful four-sided prisms, very easily soluble in water, less soluble in alcohol, not decomposed at 100° (Hofmann, *Zeitschr. f. Chem.* [2] vi. 158).

MELAPHYR. Analysis of this rock from Norheim near Kreuznach and Kokos in the Dobrudscha, are given by Laspeyres (*Jahresb.* 1865, p. 922) and Sommaruga (*ibid.* 1866, p. 978).

MELILOTIC ACID. Syn. with HYDROCOUMARIC ACID (p. 715).

MELISSIN. $C^{31}H^{64}O$.—This alcohol occurs in Canaüba wax (p. 391).

MELLITIC ACID. $C^{12}H^6O^{12}$ (Baeyer, *Ann. Ch. Pharm. Suppl.* vii. 1; Preliminary Notice, *Berl. Akad. Ber.* 1866, p. 77; *Ann. Ch. Pharm.* cxli. 271; further, *Deut. chem. Ges. Ber.* 1871, 273; *Chem. Soc. J.* [2] ix. 372).—This acid, formerly represented by the formula $C^4H^2O^4$, and regarded as bibasic, has been shown by Baeyer's investigations to be sexbasic, and to have the constitution of benzene-hexcarbonic acid, $C^6(CO^2H)^6$—that is, to consist of benzene in which all the six carbon-atoms are replaced by carboxyl.

The composition of the salts and ethers of mellitic acid, according to the six-carbon formula, may be illustrated by the following examples:

Neutral.	Acid.
$C^{12}O^{12}(NH^4)^6$	$C^{12}O^{12}H^4(NH^4)^2$
$C^{12}O^{12}(CH^3)^6$	$C^{12}O^{12}H^3K^3$
$C^{12}O^{12}(C^2H^5)^6$	$C^{12}O^{12}H^4(C^2H^5)^2$
$C^{12}O^{12}Ba''^3$	$C^{12}O^{12}H^2Cu''^3$
$C^{12}H^{12}(Al^2)^{vi}$	

Mellitic chloride, obtained by H. Müller (iii. 874) by the action of phosphorus pentachloride on mellitic acid, has the composition $C^6(COCl)^6$. Müller described it as non-volatile, but Baeyer finds that, on distilling the product in a stream of air, the mellitic chloride passes over (after the $POCl^3$ and excess of PCl^5) as a colourless oil, which solidifies to a crystalline mass on cooling. It dissolves easily in pure ether, is insoluble in water, and is slowly converted by boiling therewith into mellitic acid.

Mellitic acid is capable of yielding a large number of amidogen derivatives. Between mellitamide, $C^6(CONH^2)^6$, and mellitic acid, $C^6(COOH)^6$, there may exist by hydrogen sulphide, crystallises in rhombic tables sparingly soluble in cold water, alcohol, and ether. Its *alkali-metal salts* are very soluble and crystallisable. The *lead salt*, $(C^6H^9N^2O^5)^2Pb$, forms sparingly soluble needles; the *barium salt*, $(C^6H^9N^2O^5)^2Ba$, microscopic rhombic tables; the *silver salt* is very soluble in water, and decomposes even when its solution is heated.

Oxethyl-glycollyl-allophanic acid gives off cyanic acid when heated, and is decomposed by boiling with strong potash-ley into glycollic acid, carbonic acid, alcohol, and ammonia:

$$C^6H^{10}N^2O^5 + 5KHO = C^2H^3O^3K + 2CO^3K^2 + C^2H^6O + 2NH^3.$$

It is not decomposed by nitric or nitrous acid. Strong sulphuric acid decomposes it with evolution of carbon dioxide. By boiling with dilute sulphuric acid it is converted into a new acid, which is likewise produced, together with oxethyl-glycollyl-allophanic acid, by the action of potassium cyanate on ethyl monochloracetate. This acid is soluble in ether, uncrystallisable, forms uncrystallisable salts, and is likewise converted into glycollic acid by boiling with potash.

OXYANILINE, $C^6H^7NO = C^6H^5—O—NH^2$, is produced by heating amidosalicylic acid mixed with pumice-powder:

$$C^7H^5(NH^2)O^3 = CO^2 + C^6H^7NO.$$

When freed from a brown secondary product by means of alcohol containing acetic acid, it forms white needles, the aqueous solution of which quickly turns brown when left to itself, indigo-blue on addition of alkalis, and is decolorised again by acids. It reduces the oxides of the noble metals, forming a violet liquid. It unites with hydrochloric, hydrobromic, and hydriodic acids, forming salts which are stable only in presence of excess of acid (R. Schmitt, *Chem. Soc. J.* [2] ii. 124).

OXYBENZAMIDE. $C^7H^7NO^2 = C^6H^4(OH).CONH^2$.—Produced by boiling the aqueous solution of nitrate of diazobenzamide:

$$C^6H^3N^2.CONH^2 + H^2O = N^2 + C^6H^4(OH).CONH^2.$$

It crystallises in white prisms sparingly soluble in cold water, easily in boiling water, also in alcohol and ether. By boiling with aqueous potash it is converted into oxybenzoic acid: $C^7H^7NO^2 + H^2O = NH^3 + C^7H^6O^3$, whereas its isomeride, amidobenzoic acid, $C^6H^4NH^2.CO^2H$ (formed by reduction of nitrobenzoic acid), is not decomposed in the same manner, but only by fusion with potassium hydrate, being then resolved into carbon dioxide and aniline: $C^7H^7NO^2 = CO^2 + C^6H^7N$. Moreover, oxybenzamide is converted by nitrous acid into a diazo-compound, whereas amidobenzoic acid similarly treated is transformed into oxybenzoic acid. In like manner, paraoxybenzamide (oxydracylamide) differs from amidoparaoxybenzoic acid, and metaoxybenzamide (salicylamide) from amido-metaoxybenzoic (anthranilic) acid (Griess, *Zeitschr. f. Chem.* [2] ii. 1).

OXYBENZOIC ACID. $C^7H^6O^3 = C^6H^4(OH).CO^2H$.—In preparing this acid by the action of nitrous acid on amidobenzoic (oxybenzamic) acid (iv. 200), Gräbe a. Schultzen (*Ann. Ch. Pharm.* cxlii. 350) neutralise the boiling solution of amidobenzoic acid in 100 pts. water, after the action of the nitrous acid is complete, with levigated chalk, to prevent loss by volatilisation with the aqueous vapour, decolorise the resulting calcium salt by repeated treatment with animal charcoal, and decompose it with hydrochloric acid. Oxybenzoic acid is more advantageously prepared by fusing potassium sulphobenzoate (benzene-sulphate, benzyl-sulphite) with potassium hydrate:

$$\underset{\text{Sulphobenzoate.}}{C^6H^4\left\{\begin{matrix}SO^3K\\CO^2K\end{matrix}\right.} + \underset{\text{Hydrate.}}{KOH} = \underset{\text{Sulphite.}}{SO^3K^2} + \underset{\text{Oxybenzoate.}}{C^6H^4\left\{\begin{matrix}OH\\CO^2K\end{matrix}\right.}$$

Benzoic acid (100 grms.) is converted into sulphobenzoic acid by treatment with vapour of sulphuric anhydride; the product is made to drop through a narrow funnel into cold water; the liquid filtered from undecomposed benzoic acid is neutralised with milk of lime; the filtrate, together with the solution obtained by boiling the residual gypsum, is concentrated, and precipitated while warm with potassium carbonate; and the filtered solution of potassium sulphobenzoate is evaporated to dryness. This salt is then fused with 2½ times its weight of potassium hydrate and a little water in a silver basin; the fused mass is saturated with sulphuric acid and agitated with ether; the ethereal solution evaporated; and the residual oxybenzoic acid, after being recrystallised once or twice, with addition of animal charcoal, is finally freed from traces of benzoic acid by treatment with carbon bisulphide. By this process 100 pts. benzoic acid yield from 70 to 75 pts. oxybenzoic acid. A small quantity of a syrupy acid, probably oxysalicylic acid, $C^7H^6O^4$ (protocatechuic acid, according to Senhofer), is formed at the same time (L. Barth, *Ann. Ch. Pharm.* cxlviii. 30; *Zeitschr. f. Chem.* [2] v. 23). Amidobenzoic acid heated with potassium hydrate yields only small quantities of oxybenzoic acid: $C^7H^5(NH^2)O^2 + H^2O = NH^3 + C^7H^6O^3$ (Barth).

Ammonium Oxybenzoate, $C^7H^5O^3.NH^4$, crystallises in tufts of needles easily soluble in cold water, giving off part of their ammonia when dried in a vacuum. The *barium salt*, $(C^7H^5O^3)^2Ba$, obtained by saturating the acid with barium carbonate, is uncrystallisable. Its solution mixed with excess of baryta does not yield a salt containing $C^7H^4O^3Ba$. The *cadmium salt*, $(C^7H^5O^3)^2Cd$, forms nodular groups of indistinct needles. The *copper salt*, $(C^7H^5O^3)^2Cu + H^2O$ (air-dried), crystallises in green needles.

Oxybenzoic Ethers.—Ethyl Oxybenzoate, $C^6H^4(OH).CO^2C^2H^5$, is formed by passing hydrochloric acid gas into the alcoholic solution of the acid, and precipitating with water. It crystallises from ether and from hot water in hard tables, melting at 72°–74° (Gräbe a. Schultzen); in broad laminæ and scales melting at 67° (Barth). It distils at higher temperatures, is nearly insoluble in cold water, more soluble in hot water, also in alcohol and ether. By strong soda-ley in the cold it is converted into a white crystalline pulp of *ethylic sodium-oxybenzoate*, $C^6H^4(ONa).CO^2C^2H^5$, which is resolved into alcohol and sodium oxybenzoate by boiling its aqueous solution, and reconverted into ethylic oxybenzoate by boiling with hydrochloric acid (Gräbe a. Schultzen). According to Rosenthal (*Zeitschr. f. Chem.* [2] v. 627), ethylic oxybenzoate treated with sodium and carbon dioxide is converted into ethyl-oxybenzoic acid, $C^6H^4(OC^2H^5).CO^2H$.

Methyl-oxybenzoic Acid. $C^6H^4(OCH^3).CO^2H$.—The ethylic ether of this acid is produced by heating the ethylic ether of sodium-oxybenzoic acid with methyl iodide to 140°:

$$C^6H^4\left\{\begin{matrix}ONa\\CO^2C^2H^5\end{matrix}\right. + CH^3I = NaI + C^6H^4\left\{\begin{matrix}OCH^3\\CO^2C^2H^5\end{matrix}\right..$$

The acid produced from this ether by boiling with potash may be more easily prepared by heating 1 mol. oxybenzoic acid to 140° with 2 mol. potassium hydrate and 1 mol. methyl iodide, and decomposing the resulting methylic ether of methyl-oxybenzoic acid with potash; or, according to Körner (*Bull. Acad. Belg.* [2] xxiv. 155), by the action of carbon dioxide and sodium on methyl monobromophenate, $C^6H^4BrO.CH^3$. It crystallises from water in long needles, slightly soluble in cold, easily in hot water, alcohol, and ether, melts at 95°, and sublimes without decomposition. Its *potassium* and *ammonium salts* are easily soluble and crystallisable; the *calcium salt*, $(C^8H^7O^3)^2Ca + H^2O$, separates from the concentrated solution in needles easily soluble in hot water. The *silver salt*, $C^8H^7O^3Ag$, is a white precipitate, which crystallises from warm water in long needles.

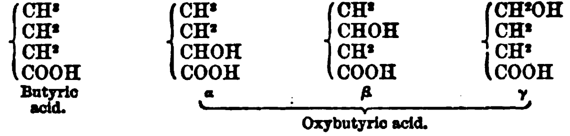
Dioxybenzoic acid, $C^7H^6O^4$ or $C^6H^3(OH)^2.CO^2H$, identical with protocatechuic acid, is produced by converting oxybenzoic acid into sulphoxybenzoic acid, $C^7H^6SO^6$, and fusing the potassium salt of the latter with potash (Barth).

Sulphoxybenzoic Acid. $C^7H^6SO^6 = C^7H^5O^3.SO^3H$ (Senhofer, *Ann. Ch. Pharm.* clii. 102).—Produced by passing vapour of sulphuric anhydride over oxybenzoic acid. On diluting the product with 10 or 12 pts. of water, removing unaltered oxybenzoic acid by repeated agitation with ether, precipitating the sulphuric acid with a slight excess of lead carbonate, mixing the filtrate with basic lead acetate, decomposing the washed precipitate with hydrogen sulphide, concentrating the filtrate strongly on the water-bath, and leaving it to itself for some time, sulphoxybenzoic acid separates in dingy yellow crusts; it may be purified by repeated treatment, after drying, with a mixture of 1 pt. alcohol and 2 pts. ether, in which the pure acid slowly dissolves. By recrystallisation from water the acid is obtained in siskin-green needles, which retain 1½ mol. H^2O when dried over sulphuric acid, give it off at 160°, and melt to a black pasty mass at 208°. It is deliquescent, very soluble in alcohol, nearly insoluble in ether; forms with ferric chloride a wine-red liquid, which is decolorised by sodium carbonate, and precipitated by basic, but not by neutral acetate of lead. The impure acid quickly becomes moist in contact with the air; but the pure acid is much less hygroscopic.

Barium Sulphoxybenzoate, $C^7H^4SO^6Ba$, forms colourless transparent prisms, which become opaque and friable on exposure to the air, and are somewhat sparingly soluble in water; the air-dried salt gives off 20·81 p. c. water at 168°; calc. for 4½H^2O, 20·36 p. c. The *acid cadmium salt*, $(C^7H^5SO^6)^2Cd + 2H^2O$, forms straw-yellow crystalline nodules. The *lead salt*, $(C^7H^3SO^6)^2Pb^3$, is obtained as a bulky precipitate, which becomes somewhat denser when left in the liquid, and dries up to a pale red amorphous mass.

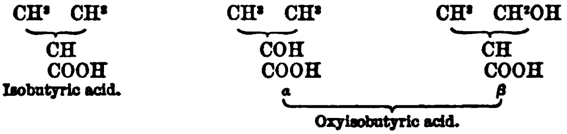
OXYBENZYL-COMPOUNDS. See TOLYL BISULPHIDE, under BENZENE HOMOLOGUES (p. 289).

OXYBUTYRIC ACID. $C^4H^8O^3$ (Morkownikoff, *Zeitschr. f. Chem.* [2] ii. 485; iv. 620. Wislicenus, *Ann. Ch. Pharm.* cxlix. 205; *Zeitschr. f. Chem.* [2] iv. 680; v. 325).—The general formula of this acid may be resolved into five different structural formulæ, three of which contain only a single chain of carbon-atoms, and may be regarded as derivatives of ordinary butyric acid:



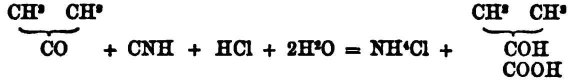
$$\underset{\text{Butyric acid.}}{\left\{\begin{array}{l}CH^3\\CH^2\\CH^2\\COOH\end{array}\right.}\qquad\underbrace{\underset{\alpha}{\left\{\begin{array}{l}CH^3\\CH^2\\CHOH\\COOH\end{array}\right.}\qquad\underset{\beta}{\left\{\begin{array}{l}CH^3\\CHOH\\CH^2\\COOH\end{array}\right.}\qquad\underset{\gamma}{\left\{\begin{array}{l}CH^2OH\\CH^2\\CH^2\\COOH\end{array}\right.}}_{\text{Oxybutyric acid.}}$$

while the remaining two may be derived from isobutyric acid:



$$\underset{\text{Isobutyric acid.}}{\begin{array}{c}\underbrace{CH^3\ \ CH^3}\\CH\\COOH\end{array}}\qquad\underbrace{\underset{\alpha}{\begin{array}{c}\underbrace{CH^3\ \ CH^3}\\COH\\COOH\end{array}}\qquad\underset{\beta}{\begin{array}{c}\underbrace{CH^3\ \ CH^2OH}\\CH\\COOH\end{array}}}_{\text{Oxyisobutyric acid.}}$$

Of these five oxybutyric acids two have been known for some time, namely α-oxyisobutyric and α-oxybutyric acids. The former is produced by the action of moist silver oxide on bromo-isobutyric acid (Morkownikoff, *Ann. Ch. Pharm.* cxlvi. 339). The same structure belongs to Städeler's acetonic acid, produced by the action of hydrocyanic and hydrochloric acids on acetone (p. 28):

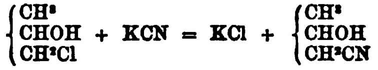


$$\begin{array}{c}\underbrace{CH^3\ \ CH^3}\\CO\end{array} + CNH + HCl + 2H^2O = NH^4Cl + \begin{array}{c}\underbrace{CH^3\ \ CH^3}\\COH\\COOH\end{array}$$

and to Frankland a. Duppa's dimethoxalic acid (iv. 274). Wurtz's butylactic acid (i. 688), obtained by oxidation of amylene glycol, is also, according to Friedel a. Machuca (*ibid.* cxx. 279), identical with acetonic acid. There are therefore four modes of formation of α-oxyisobutyric acid, all of which yield it in the crystalline state.

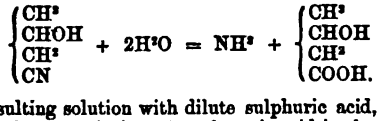
Another oxybutyric acid, also crystalline, was obtained by Friedel a. Machuca (iv. 296), and by Naumann (*Ann. Ch. Pharm.* cxix. 115), by the action of silver oxide on normal bromobutyric acid. Now when hydrogen is replaced by chlorine or bromine in organic molecules already containing negative elements, the replacement generally takes place, at least in the first instance, in the immediate neighbourhood of the negative atoms already present: thus aldehydes are converted into acid chlorides; ethyl chloride, $CH^3.CH^2Cl$, into ethylidene dichloride, $CH^3.CHCl^2$; propionic acid, $CH^3—CH^2—COOH$, into α-chloropropionic acid, $CH^3—CHCl—COOH$, &c. In like manner, normal butyric acid, $CH^3—CH^2—CH^2—CO^2H$, acted upon by bromine will most probably yield a bromobutyric acid having the constitution $CH^3—CH^2—CHBr—CO^2H$, and this acid treated with silver oxide will be converted into *α-oxybutyric acid*, $CH^3—CH^2—CHOH—CO^2H$ (Wislicenus).

A third modification, viz. *β-oxybutyric acid*, which is non-crystalline, has recently been obtained by Morkownikoff and by Wislicenus:—1. From propylene-hydroxychloride, by converting that compound into the corresponding hydrocyanide by heating with potassium cyanide, and boiling the alcoholic solution of the product with caustic potash as long as ammonia continues to escape:



$$\left\{\begin{array}{l}CH^3\\CHOH\\CH^2Cl\end{array}\right. + KCN = KCl + \left\{\begin{array}{l}CH^3\\CHOH\\CH^2CN\end{array}\right.$$

and



$$\left\{\begin{array}{l}CH^3\\CHOH\\CH^2\\CN\end{array}\right. + 2H^2O = NH^3 + \left\{\begin{array}{l}CH^3\\CHOH\\CH^2\\COOH.\end{array}\right.$$

By acidulating the resulting solution with dilute sulphuric acid, agitating with ether, and evaporating the ethereal solution, β-oxybutyric acid is obtained in the form of a syrup, which may be purified by conversion into a lead salt, and separation with hydrogen sulphide (Morkownikoff).

2. By addition of hydrogen to acetyl-acetic acid, $C^2H^3(C^2H^3O)O^2$:

$$\left\{\begin{array}{l}CH^3\\CO\\CH^2\\COOH\end{array}\right. + H^2 = \left\{\begin{array}{l}CH^3\\CHOH\\CH^2\\COOH\end{array}\right.$$

The ethylic ether of acetyl-acetic acid (Geuther's ethyl-diacetic acid, p. 601) treated with water and sodium-amalgam is rapidly converted into the sodium salt of β-oxybutyric acid:

$$\left\{\begin{array}{l}CH^3\\CO\\CH^2\\COOC^2H^5\end{array}\right. + 2H^2O + Na^2 = NaHO + C^2H^5OH + \left\{\begin{array}{l}CH^3\\CHOH\\CH^2\\COONa\end{array}\right.$$

By slightly acidulating the alkaline liquid with hydrochloric acid, again neutralising with sodium carbonate, evaporating to a syrup, separating the sodium chloride which crystallises out, evaporating to dryness, digesting the residue with strong alcohol, and leaving the solution to cool, sodium β-oxybutyrate is obtained, and may be purified by repeated crystallisation from alcohol. By decomposing this sodium salt with sulphuric acid, agitating the solution with ether, and evaporating, β-oxybutyric acid is obtained as a slightly coloured viscid syrup, which quickly absorbs water from the air, and shows no tendency to crystallise. It volatilises somewhat readily with vapour of water, and decomposes when heated to 120°–130°, yielding a thickish acid watery distillate, which on cooling deposits snow-white crystals, having the composition $C^4H^6O^2$, and exhibiting nearly the properties of crotonic acid obtained from allyl cyanide (p. 509).

Sodium β-oxybutyrate, $C^4H^7O^3Na$, prepared as above forms anhydrous crusts made up of very soft sharply pointed crystals; it is soluble in water and in alcohol, and very deliquescent. The *silver salt*, $C^4H^7O^3Ag$, separates on mixing the solution of the sodium salt with silver nitrate, in snow-white, capillary, interlaced crystals. The calcium, copper, lead, and zinc salts, which are very soluble and amorphous, are obtained by boiling the acid with the corresponding carbonates (Wislicenus).

OXYCANNABIN. $C^8H^6O^2$.—A neutral crystalline substance obtained by the action of nitric acid on the resinous extract of Indian hemp. (See CANNABIS, p. 391.)

OXYCINNAMIC ACID. See CINNAMIC ACID (p. 470).

OXYDRACYLAMIC ACID. Syn. with Paramidobenzoic acid. See BENZOIC ACID (p. 320).

OXYGEN. *Preparation.*—1. Robbins (*Pharm. J. Trans.* [2] v. 456) recommends the decomposition of a pulverised mixture of 3 mol. barium peroxide and 1 mol. potassium dichromate with dilute sulphuric acid, whereby oxygen is abundantly evolved at ordinary temperatures.—2. Carlevaris (*Bull. Soc. Chim.* [2] iv. 255) heats a mixture of manganese dioxide and sand to incipient redness, whereby manganous silicate is produced, and half the oxygen of the manganese dioxide is evolved.—3. Chloride of lime in solution heated with a small quantity of recently prepared *cobalt peroxide*, is completely resolved into calcium chloride and oxygen (less easily by nickel peroxide). A concentrated solution of strong chloride of lime (35 p. c.) filtered to prevent frothing, yields, when heated with 0·1 to 0·5 p. c. cobalt peroxide, a volume of oxygen from 25 to 30 times as great as that of the liquid, and always rather more than the calculated quantity, probably in consequence of absorption of oxygen from the air. The remaining peroxide can always be used again. The same result is obtained by mixing the chloride of lime solution with a small quantity of an ordinary cobalt salt. It is probable that several peroxides of cobalt exist, and that the reaction depends upon the alternate formation and partial reduction of a higher oxide, or on the formation of a cobaltic or percobaltic hypochlorite, which is subsequently resolved into cobaltous chloride and oxygen (Fleitmann, *Ann. Ch. Pharm.* cxxxiv. 64). These observations have been confirmed by Reinsch (*Zeitschr. f. Chem.* [2] ii. 31), and similar observations have been made by Böttger, who likewise observes that cupric oxide and ferric hydrate decompose chloride of lime with violence, even at 60°, both remaining unaltered (*J. pr. Chem.* xcv. 309, 375; *Jahresb.* 1865, p. 119). Stolba (*ibid.* xcvii. 309) recommends that the chloride of lime in Fleitmann's process be used in the form of a stiff paste, with addition of a small quantity of cupric nitrate or chloride and a few small lumps of paraffin; by this means the frothing of the liquid is prevented. Winkler (*J. pr. Chem.* xcviii. 340) passes chlorine into thick milk of lime containing a few drops of solution of cobaltous chloride, and passes the evolved oxygen through a wash-bottle containing milk of lime, to remove a small quantity of chlorine with which it is mixed.

with ether, and the aqueous solution of the ethereal extract is precipitated with boiling baryta-water, whereby pyromellitic and trimellitic acids are precipitated, while isophthalic acid remains in solution. The precipitate is decomposed by sulphuric acid, the filtrate concentrated, and the crystalline mass which separates on cooling is fused and digested with pure ether, which dissolves the trimellitic acid, leaving the pyromellitic acid undissolved.

The decomposition of hydropyromellitic acid by sulphuric acid may be represented by the following equation:

$$C^{10}H^{10}O^8 + 2SO^4H^2 - 4H^2O - 2SO^2 = \begin{cases} C^{10}H^6O^8, & \text{Pyromellitic acid} \\ CO^2 + C^9H^6O^6, & \text{Trimellitic acid} \\ 2CO^2 + C^8H^6O^4, & \text{Isophthalic acid.} \end{cases}$$

Trimellitic Acid. $C^9H^6O^6 = C^6H^3(CO^2H)^3$.—This acid, dissolved as above by ether, is purified by conversion into a lead salt in the manner already described (p. 811). It is moderately soluble in water and ether, and crystallises from aqueous solution by slow evaporation in nodular groups of indistinct crystals. It melts at 216°, and when more strongly heated does not sublime, but distils in oily drops, which solidify on cooling to nodular groups of concentric needles. In this respect it bears considerable resemblance to isopyromellitic acid, which however melts at 238°, and solidifies from the oil obtained on distilling it, in needles and isolated crystals. These characters, however, are distinctly exhibited only when the respective acids are pure. The two acids are further distinguished by the different solubilities of their barium salts, isopyromellitic acid giving a precipitate with barium chloride, whereas this reagent does not produce a precipitate even with the ammonium salt of trimellitic acid.

Ammonium trimellitate is easily soluble in water, and crystallises in concentric needles from the concentrated solution. The *barium salt* is sparingly soluble, and separates on mixing the ammonium salt with barium chloride, especially on heating, in crystalline nodules, exhibiting, after drying over sulphuric acid, the composition $(C^9H^3O^6)^2Ba^3 + 3H^2O$. With *lead acetate*, trimellitic acid forms a flocculent precipitate nearly insoluble in acetic acid. *Silver nitrate* forms, especially on addition of ammonia, a granular precipitate, which dissolves when heated, and reappears on cooling.

The acids above described belong to two classes, the benzocarbonic and the hydrobenzocarbonic acids. Of the benzocarbonic acids, as already observed, twelve are possible, and eleven have actually been obtained. These are arranged by Baeyer as ortho-, meta-, and para- compounds (AROMATIC SERIES, p. 197) as follows:

	Ortho-series.	*Meta-series.*	*Para-series.*
$C^6(CO^2H)^6$	1 2 3 4 5 6 Mellitic acid.		
$C^6H(CO^2H)^5$	1 2 3 4 5 Unknown.		
$C^6H^2(CO^2H)^4$	1 2 3 4 Mellophanic acid.	1 2 3 5 Prehnitic.	1 2 4 5 Pyromellitic acid.
$C^6H^3(CO^2H)^3$	1 2 3 Hemimellitic acid.	1 2 4 Trimesic acid..	1 3 5 Trimellitic acid.
$C^6H^4(CO^2H)^2$	1 2 Phthalic acid.	1 3 Isophthalic acid.	1 4 Terephthalic acid.
$C^6H^5CO^2H$	1 Benzoic acid.		

Of the hydrobenzo-carbonic acids, two were previously known, viz. hydrobenzoic acid, $C^7H^{10}O^2$, and hydrophthalic acid, $C^8H^8O^4$; and four more have been added to the list by Baeyer's recent investigations, viz. hydromellitic acid, $C^{12}H^{12}O^{12}$, hydropyromellitic, hydroprehnitic, and hydromellophanic acids, $C^{10}H^{10}O^8$. The difference of structure of mellitic and hydromellitic acid may be represented by the following formulæ, in which the symbol X stands for CO^2H:

in ether, and especially in benzol. Heated with potash it yields potassium oxypicrate and ethylic alcohol (Stenhouse).

OXYQUINONE. $C^6H^4O^3 = C^6H^4\left\{\begin{matrix}O\\O\end{matrix}\right.O$ (Malin, *Ann. Ch. Pharm.* cxli. 345).—A compound produced by fusing rufigallic acid with potash:

$$C^7H^4O^4 + O = C^6H^4O^3 + CO^2.$$

On saturating the product with dilute sulphuric acid, agitating the filtered solution with ether, and leaving the ether to evaporate, oxyquinone is obtained in hydrated yellowish crystals containing $C^6H^4O^3.H^2O$. After being pressed to remove the brown mother-liquor, and recrystallised from boiling water, it forms soft straw-yellow microscopic needles, slightly soluble in cold, easily in boiling water, also in alcohol and ether, having a faint acid reaction, and not volatile. The aqueous solution when heated reduces silver nitrate and alkaline cupric solutions; in the dilute state it colours ferric chloride violet, afterwards blue-green. Oxyquinone, like quinone, has but slight combining tendencies; nevertheless it absorbs dry ammonia gas and forms a yellowish precipitate with lead acetate. It is not converted into quinone by nascent hydrogen.

OXYSULPHOBENZIDE. $C^{12}H^{10}SO^4 = \left.\begin{matrix}C^6H^4SO^2\\C^6H^4\end{matrix}\right\}O^2$ (Glutz, *Ann. Ch. Pharm.* cxlvii. 52; *Jahresb.* 1867, p. 635).—Produced by the action of strong sulphuric acid on crystallised phenol. It dissolves easily in boiling water, also in alcohol and ether, and crystallises therefrom in groups of thick needles, fusible at a moderate heat, decomposing at a higher temperature. It unites both with bases and with acids. Its *ammoniacal* solution deposits short prisms of the salt $C^{12}H^9(NH^4)SO^4$; the *sodium salt*, $C^{12}H^9NaSO^4$, forms short prisms easily soluble in water and in boiling alcohol. The *acetate*, $C^{12}H^8(C^2H^3O)^2SO^4$, obtained by heating oxysulphobenzide with excess of acetyl chloride to 130°, crystallises from alcohol in needles, decomposing at the boiling heat into oxysulphobenzide and acetic acid. *Nitro-oxysulphobenzide*, $C^{12}H^8(NO^2)^2SO^4$, crystallises in scales, and forms with the alkalis and alkaline earths easily soluble deep yellow compounds, *e.g.* $C^{12}H^6Na^2(NO^2)^2SO^4$ and $C^{12}H^6Ba(NO^2)^2SO^4$. By phosphorus iodide in presence of a little water, it is converted into the compound $C^{12}H^8(NH^2)^2SO^4.2HI$, which forms crystals easily soluble in water and in alcohol; caustic soda decomposes it, separating the corresponding base as a white precipitate quickly turning brown on exposure to the air.

OXYVALERIC ACID. $C^5H^{10}O^3 = C^4H^8(OH).CO^2H$. *Valerolactic Acid.*—Produced by heating bromovaleric acid with silver oxide and water, and purified by converting it into calcium salt, precipitating the latter with alcohol, converting it into zinc salt, and decomposing this salt with hydrogen sulphide. Crystallises by evaporation over sulphuric acid in large rectangular tables, not deliquescent, but very soluble in water, alcohol, and ether; melts at 80°, and volatilises with vapour of water, also at 100° in the air-bath. The *sodium salt*, $C^5H^9O^3Na$, the *calcium salt*, $(C^5H^9O^3)^2Ca + H^2O$, and the *zinc salt*, $(C^5H^9O^3)^2Zn$, are soluble in water and crystallisable. The *copper salt*, $(C^5H^9O^3)^2Cu + H^2O$, separates on mixing the calcium salt with cupric acetate, in light green prisms which become anhydrous at 170°. The *silver salt*, $C^5H^9O^3Ag$, is a bulky precipitate, separating from hot water in feathery crystals (Clark a. Fittig, *Ann. Ch. Pharm.* cxxxix. 199).

OZONE. Soret has determined the density of ozone by comparing its rate of diffusion with that of chlorine. His experiments confirm the result previously obtained by Andrews (iv. 301), that the density of ozone is 1½ time as great as that of ordinary oxygen (*Ann. Ch. Phys.* [4] xiii. 257; *Jahresb.* 1867, p. 123). Another, but less exact method, depending on the absorption of ozone by oil of turpentine, yielded results tending to the same conclusion (*Ann. Ch. Phys.* [4] vii. 113; *Jahresb.* 1865, p. 120).

On the properties of ozone and ozonides, see Schönbein (*J. pr. Chem.* xcv. 469; cii. 145, 155, 164; cv. 226; *Jahresb.* 1865, p. 121; 1867, p. 132; 1868, p. 136). On ozone and so-called *antozone*, see v. Babo a. Claus (*Ann. Ch. Pharm.* cxl. 348; *Jahresb.* 1866, p. 98); Weltzien (*Ann. Ch. Pharm.* cxxxviii. 129; *Jahresb.* 1866, p. 99); C. Hoffmann (*Pogg. Ann.* cxxxii. 607; *Jahresb.* 1867, p. 130).

P. J. Hollmann finds that 1 gram of ozone, in passing to the state of ordinary oxygen, gives off 355·5 units of heat (*Arch. néerland.* iii. 260; *Jahresb.* 1868, p. 136).

According to O. Loew (*Zeitschr. f. Chem.* [2] vi. 65, 269), ozone is produced in active as well as in slow combustion. Air which had passed through the flame of a Bunsen's burner smelt strongly of ozone, turned guaiac paper blue, and quickly separated iodine from potassium iodide.

On the existence of ozone in the air, see ATMOSPHERE (p. 233).

P

PACHNOLITE. A reddish-white quadratic variety of this mineral, of sp. gr. 2·74 to 2·76, and the hardness of cryolite, was found by Hagemann (*Sill. Am. J.* [2] xli. 119) to have nearly the composition indicated by the formula $2(\frac{2}{3}Ca . \frac{1}{3}Na^2)F^2 . Al^2F^6 + 2H^2O$. On the crystalline form and optical properties of rhombic pachnolite, see Descloizeaux (*ibid.* xliii. 271; *Jahresb.* 1867, p. 1009).

PALICOUREA. *Palicourea Marcgravii*, a Brazilian rubiaceous plant, contains as peculiar principles: 1. A small quantity of an oily narcotic acid substance, myoctonic acid, obtained by distilling the acidulated juice.—2. Palicoureic acid, an iron-greening tannic acid, insoluble in water and subliming in needles.—3. Palicourine, a volatile organic base, forming a crystallisable nitrate and sulphate.—4. Several resins (Peckolt, *Arch. Pharm.* cxxvii. 93).

PALLADIUM. On the separation of this metal from Petersburg platinum-residues, see Rössler (*Bull. Soc. Chim.* [2] vi. 233; *Jahresb.* 1866, p. 275).

On the occlusion of hydrogen by palladium, see GASES, ABSORPTION OF (p. 634).

According to Wöhler (*Ann. Ch. Pharm.* cxl. 144), the quantitative separation of palladium from copper is best effected by precipitating the copper as white sulphocyanate, the solution of palladium chloride being saturated with sulphurous anhydride and the copper precipitated by potassium sulphocyanate. The precipitation of palladium by mercuric cyanide is not exact.

Palladammonium Salts.—The colourless solution of palladammonium chloride in ammonia, which contains tetrammonio-palladious chloride, $4NH^3 . PdCl^2$, or ammono-palladammonium chloride, $N^2[H^4(NH^4)^2Pd'']Cl^2$, gives off ammonia when heated, the liquid on cooling depositing a mixture of the chlorides of palladammonium and ammopalladammonium. If, on the other hand, the palladammonium salt be first moistened with alcohol, and then treated with concentrated ammonia, the mass turns white, and is converted into the ammopalladammonium salt. This latter dissolves when heated, and the solution, evaporated at about 90°, first deposits yellow palladammonium chloride, together with monoclinic prisms of ammopalladammonium chloride, and finally honey-yellow crystals of hydrated palladammonium chloride, $N^2H^6PdCl^2 + H^2O$. These crystals are combinations of a quadratic octohedron with a right four-sided prism. They effloresce in contact with the air to opaque pseudomorphs of palladammonium chloride; give off ammonia at 140°; and leave metallic palladium when more strongly heated. The salt is insoluble in alcohol. The aqueous solution quickly decomposes, especially when heated, depositing ordinary palladammonium chloride. Soda precipitates palladamine without evolution of ammonia. Acids separate the ordinary yellow chloride (Baubigny, *Ann. Ch. Pharm. Suppl.* iv. 253).

PALMITIC ACID. $C^{16}H^{32}O^2$.—By treating sodium palmitate with hypochlorous acid, a chlorinated oil is obtained, probably *dichloropalmitic acid*, which, when treated with alcoholic potash, yields a decomposition-product separating from alcohol in flat nodules (W. Schlebusch, *Ann. Ch. Pharm.* cxli. 322).

PALMITOLIC ACID. $C^{16}H^{28}O^2$ (Schröder, *Ann. Ch. Pharm.* cxliii. 22).—An acid produced by heating hypogæic dibromide (dibromopalmitic acid), $C^{16}H^{30}Br^2O^2$, with alcoholic potash to 170°–180° in a sealed tube for three or four days. The product treated with a little alcohol, filtered, diluted with water, and decomposed with hydrochloric acid, yields palmitolic acid as a crystalline mass, which when pressed and recrystallised from alcohol, forms colourless slender silky needles, melting at 42°, insoluble in water, but easily soluble in alcohol and ether. The acid is monobasic. Its alkali-metal salts are obtained by direct saturation and evaporation. The *potassium* and *sodium salts* are amorphous; the *ammonium salt* forms small indistinct crystals. The *silver salt*, $C^{16}H^{27}O^2Ag$, is formed, by precipitating an alcoholic solution of the acid with silver nitrate and gradual addition of ammonia, as a white amorphous powder easily blackened by light. The *barium salt* is obtained in like manner, by precipitation with a concentrated solution of barium acetate in dilute alcohol, as a white precipitate, which dissolves only in boiling alcohol, and separates in the granulo-crystalline form on cooling. The *copper salt* is a blue-green precipitate.

Palmitolic acid unites with 1 mol. *bromine*, forming the dibromide, $C^{16}H^{28}Br^2O^2$ (dibromo-hypogæic acid); with excess of bromine in sunshine (with partial decomposition and evolution of hydrobromic acid) it forms the tetrabromide, $C^{16}H^{28}Br^4O^2$ (tetrabromopalmitic acid), which crystallises from alcohol in light yellow laminæ.

Monobromopalmitolic acid, $C^{16}H^{27}BrO^2$, is produced by the action of boiling alcoholic potash on monobromo-hypogæic dibromide (p. 727) according to the equation:

$$C^{16}H^{28}Br^2O^2 + 2KHO = C^{16}H^{27}BrO^2 + 2KBr + 2H^2O.$$

It has been obtained only in an impure state, as a solid dark brown mass melting at 31°, heavier than water, soluble in alcohol and ether.

PALMITOXYLIC ACID, $C^{16}H^{28}O^4$, is produced, together with suberic acid and suberic aldehyde, by gradually adding fuming nitric acid to pamitolic acid, assisting the action at first by a gentle heat:

$$\underset{\substack{\text{Palmitolic}\\\text{acid.}}}{2C^{16}H^{28}O^2} + 7O = \underset{\substack{\text{Palmitoxylic}\\\text{acid.}}}{C^{16}H^{28}O^4} + \underset{\substack{\text{Suberic}\\\text{acid.}}}{C^8H^{14}O^4} + \underset{\substack{\text{Suberic}\\\text{aldehyde.}}}{C^8H^{14}O^3}$$

The suberic acid is dissolved out of the product by repeated boiling with water; the washed residue is dissolved in hot alcohol; and the lower dark-coloured oily layer of the filtrate, consisting chiefly of suberic aldehyde, is separated after cooling from the supernatant yellow solution of palmitoxylic acid. The crystalline mass which remains on evaporating this solution, when pressed between filtering-paper and recrystallised from hot absolute alcohol, yields pure palmitoxylic acid in iridescent yellowish laminæ, melting at 64°, insoluble in water, easily soluble in alcohol and ether. It is monobasic. The *silver salt*, $C^{16}H^{27}O^4Ag$, obtained from the sodium salt by precipitation, is white, nearly insoluble in water, turns dark violet when exposed to light, and may be heated to 150° without decomposition.

PANATOMS. G. Hinrichs has endeavoured to reduce the chemistry of the present day to a system of atomic mechanics, starting from the hypothesis that all the elements are formed of a single primary substance, pantogen, the atoms of which are regarded as material points, and as equal to one another. For the development of the system we must refer to the original treatise: *Atomechanik, oder die Chemie eine Mechanik der Panatome*, 4to, Iowa, 1867. A short abstract of it is given in the *Jahresbericht für Chemie*, 1867, p. 20.

PAPAVERINE. This base has been re-examined by Hesse (*Ann. Ch. Pharm.* cliii. 75), who prepares it from the precipitate P, obtained from aqueous opium extract, as described under OPIUM-BASES (p. 883). This precipitate digested with excess of oxalic acid yields crystalline oxalate of papaverine. It is better, however, first to dissolve the precipitate in acetic acid, remove thebaine by means of tartaric acid, precipitate the mother-liquor of the tartrate with ammonia, and treat the resinous precipitate with a small quantity of alcohol, whereby it is gradually converted into crystals, while an amorphous base passes into the solution. The crystals are dissolved in excess of oxalic acid, and the oxalate is purified by repeated crystallisation from boiling water, till it dissolves without colour in strong sulphuric acid. The oxalic acid is then removed by calcium chloride, and the base is precipitated by ammonia, and obtained pure by recrystallisation from hot alcohol.

Papaverine forms delicate colourless prisms, tasteless, without action on litmus, melting at 147°, turning reddish, and finally decomposing at a higher temperature. According to Merck (iv. 338), it assumes a deep blue colour when strong sulphuric acid is poured upon it. According to Hesse, on the other hand, pure papaverine dissolves without colour in strong sulphuric acid at ordinary temperatures, but the solution when heated becomes dark violet, like a similar solution of codamine or laudanine (pp. 480, 774). Papaverine which had not been completely purified by oxalic acid dissolved in strong sulphuric acid with very dark colour. Papaverine dissolves in acetic acid, but does not neutralise it; dilute sulphuric, nitric, or hydrochloric acid added to this solution, produces a milky turbidity and ultimate precipitation of the sulphate, nitrate, or hydrochloride of papaverine; the chlorides of sodium and calcium act in like manner, precipitating papaverine as hydrochloride; sodium nitrate precipitates the nitrate. With a solution of the acetate of a certain degree of dilution, the hydrochloride and nitrate are obtained in fine crystals. Potash and soda produce in the acetate solution a resinous precipitate, which soon becomes crystalline, and is insoluble in excess of the reagent.

Papaverine contains, according to the mean of Hesse's analysis, 71·77 p. c. carbon, 6·02 hydrogen, and 4·26 nitrogen, agreeing with the formula $C^{21}H^{21}NO^4$ (71·76 C, 5·98 H, and 3·99 N). Former analyses by Merck and Anderson (iv. 338) gave a smaller proportion of carbon (70·47–70·71 p. c.), leading to the formula $C^{20}H^{21}NO^4$. Hesse's analysis of several of the salts of papaverine gave results in accordance with his formula of the base. These salts dissolve in strong sulphuric acid without coloration.

The name *papaverine* has also been applied by Deschamps d'Avallon (*Ann. Ch. Phys.* [4] i. 453) to another base (better called pseudopapaverine), extracted from the dried capsules of *Papaver somniferum*. It is described as colourless, inodorous, bitter, acid to test-paper; more soluble in hot water than in cold; insoluble in ether and in chloroform; crystallising from alcohol in short nacreous needles; precipitated from solution in hydrochloric acid by mercuric chloride. A solution of iodine in potassium iodide colours it in aqueous solution blue, and forms a brown precipitate with the solution in hydrochloric acid.

PAPAVEROSINE. A substance obtained from the same dried poppy capsules, after exhaustion with water, by digesting them with alcohol of 56 p. c., treating the alcoholic extract with ether, dissolving the ethereal extract in hydrochloric acid, and repeatedly crystallising the base precipitated by magnesia from alcohol. It is colourless, inodorous, nearly tasteless, slightly alkaline; soluble in alcohol, ether, chloroform, hot olive oil, and benzol; does not crystallise from ether or chloroform, but separates from the other solvents in prisms apparently monoclinic. Strong sulphuric acid colours it violet, changing to red when heated, and to dark orange on addition of a little nitric acid. Its solution gives a whitish precipitate with platinic chloride; yellow with potassium chromate and with solution of iodine in potassium iodide; white with potassio-mercuric iodide, ammonium molybdate, barium peroxide, potassium ferrocyanide and ferricyanide (Deschamps, *loc. cit.*).

PARA. Respecting the meaning of this prefix in the AROMATIC SERIES, see page 798.

PARABANIC ACID, $C^3H^2N^2O^3$, is obtained in crystals by heating uric acid with manganese dioxide and water, and gradually adding sulphuric acid as long as any action takes place (Wheeler, *Bull. Soc. Chim.* [2] vii. 521); also by heating uric acid with potassium or sodium nitrite, adding sulphuric acid, and evaporating over the water-bath (Gibbs, *Deut. chem. Ges. Ber.* 1867, p. 341). Parabanic acid heated with potassium permanganate in presence of sulphuric acid is ultimately converted into carbon dioxide and ammonia: $C^3H^2N^2O^3 + 2H^2O + O = 3CO^2 + 2NH^3$ (Gibbs).

PARACONIC ACID. An acid isomeric with itaconic acid, produced by heating itamonochloropyrotartaric acid with water. (See ITACONIC ACID, p. 760.)

PARACOUMARIC ACID. $C^9H^8O^3$ (Hlasiwetz, *Ann. Ch. Pharm.* cxxxvi. 31).—This acid, isomeric with coumaric acid (p. 498), is extracted by ether from aloes previously exhausted with water containing sulphuric acid. After repeated crystallisation from weak spirit, with addition of animal charcoal, it forms sickle-shaped or furcate needles, slightly soluble in cold, more freely in boiling water, most easily in warm alcohol or ether. It is nearly tasteless, has a strong acid reaction; melts at 179°–180°; produces a dark golden-brown coloration with ferric chloride in alcoholic solution; does not reduce either silver nitrate or an alkaline cupric solution. It is monobasic and forms crystalline salts. $C^9H^7O^3(NH^4) + H^2O$ crystallises in monoclinic tables; $(C^9H^7O^3)^2Cd + 3H^2O$ in stellate groups of needles; $(C^9H^7O^3)^2Cu + 6H^2O$ in sparingly soluble greenish-blue needles; $C^9H^7O^3Ag$ is a white bulky precipitate.

Paracoumaric acid is converted by sodium-amalgam into hydroparacoumaric acid (p. 716), and by nitric acid, or by fusion with potash, into paraoxybenzoic acid, just as coumaric acid is converted into salicylic acid (p. 498).

PARADATISCETIN. $C^{15}H^{10}O^6$.—A compound isomeric with datiscetin (ii. 306) and luteolin, produced by fusing quercetin with potash, and separated, on supersaturating the fused mass with hydrochloric acid, as a flocculent substance, which crystallises from very weak spirit in yellowish needles. It dissolves easily and with acid reaction in dilute alcohol, less easily in ether, and is nearly insoluble in water; the alcoholic solution is coloured violet by ferric chloride, yellow by potash, turning green in contact with the air, red or red-brown by aqueous chlorine or bromine. Silver nitrate and alkaline cupric solution are reduced when heated with it. Boiled with the carbonates of alkaline earths, it yields hydrated salts, which crystallise in long needles; the barium salt dried at 100° is $(C^{15}H^9O^6)^2Ba + 2H^2O$; the strontium salt, $(C^{15}H^9O^6)^2Sr + 2H^2O$. Paradatiscetin fused with potash yields phloroglucin, but neither quercetic nor protocatechuic acid (Hlasiwetz a. Pfaundler, *J. pr. Chem.* xciv. 65; *Jahresb.* 1864, p. 563).

The formation of cinnabar under the conditions above mentioned does not take place in presence of strontium, calcium, or magnesium salts, but is accelerated by copper or zinc salts. When 1 mol. mercuric chloride is mixed with 4 mol. sodium hyposulphite and 4 mol. zinc sulphate in very dilute solution, and the mixture is heated to 45° or 50° for about sixty hours, three-fourths of the mercury is separated from the neutral liquid as dark red crystalline cinnabar, the rest at a higher temperature as black amorphous sulphide. If barium chloride be used instead of zinc sulphate, barium sulphate separates together with the cinnabar. In the ordinary mode of preparing cinnabar in the wet way, the transformation of the amorphous sulphide depends upon its successive solution in the alkaline sulphide, from which it separates in the crystalline form. The presence of sodium hyposulphite does not facilitate, but rather hinders this transformation (H. Fleck, *J. pr. Chem.* xcix. 247).

The solubility of mercuric sulphide in the sulphides of the alkali-metals and alkaline-earth metals may be made available for the extraction of the sulphide from its gangue, and especially for the valuation of poor cinnabar ores (containing 2 to 3 p. c. cinnabar). The best solvent for the purpose is a solution of barium sulphide, containing about 50 grms. of barium in a litre, obtained by dissolving crude barium sulphide in water, and crystallising out the greater part of the barium hydrate. The mercuric sulphide is precipitated from the solution of hydrochloric acid (whereby barium chloride is obtained as a secondary product), and decomposed in the ordinary way. For the assay of poor bituminous ores, the bituminous matter must first be extracted by benzol, the ore then well dried and exhausted with barium sulphide, and the precipitate thrown down by hydrochloric acid freed from admixed sulphur by digestion with carbon bisulphide (Wagner, *J. pr. Chem.* xcviii. 23; *Jahresb.* 1866, p. 834).

Cinnabar digested for a day with excess of a solution of *iodine in potassium iodide* is converted into potassio-mercuric iodide: $HgS + 2KI + I^2 = 2KI.HgI^2 + S$. The diminution of the free iodine affords a measure of the quantity of mercury dissolved (Wagner, *loc. cit.*).

The black precipitate formed in mercurous salts by *hydrogen sulphide*, or colourless *ammonium sulphide*, is not a definite compound, but a mixture of mercury and mercuric sulphide, from which nitric acid extracts the metallic mercury, forming either a mercurous or a mercuric salt, and in the latter case the white double compound $Hg(NO^3)^2.2HgS$. This double compound is nearly insoluble in nitric acid, and forms with hydrochloric acid the yellow compound $HgCl^2.2HgS$, which decomposes when heated in the liquid, with formation of sulphuric acid and separation of sulphur; sulphuric acid of medium strength converts it into the white salt, $HgSO^4.2HgS$. Mercuric sulphide, which under ordinary circumstances is insoluble in nitric acid, is likewise converted by prolonged heating with that acid into the white compound $Hg(NO^3)^2.2HgS$. Mercuric sulphide is insoluble in sodium sulphydrate, and consequently its solution in sodium sulphide is precipitated by hydrogen sulphide or ammonium sulphydrate. It appears from the preceding that the separation of mercury as sulphide from other sulphides of the same group by nitric acid is exact only when the mercury is present as mercuric sulphide (Barfoed, *Bull. Soc. Chim.* [2] iii. 183).

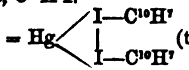
MERCURY-RADICLES, ORGANIC. *Mercuric ethide* is rapidly decomposed at temperatures near its boiling point by carbon oxysulphide, metallic mercury being separated, and a liquid having a strong alliaceous odour being formed, probably ethyl thiopropionate (Than, *Zeitschr. f. Chem.* [2] iv. 56).

Mercuric acetoxymethide, $C^3H^6O^2Hg = Hg\begin{cases}C^2H^3O^2\\CH^3\end{cases}$, is produced by heating mercuric methide with acetic acid to 120°–130° in a sealed tube. It crystallises from hot glacial acetic acid in shining, white, thin, rhombic tables, melting at 142°-143°, having an offensive and very persistent odour, nearly insoluble in boiling water and cold acetic acid, more soluble in hot acetic acid and in alcohol. It volatilises with vapour of water, and reacts with hydrochloric acid, ammonium sulphide, and iodine, like the corresponding compounds of the aromatic series described below. *Mercuric acetoxethide* resembles the methyl-compound, and melts at 178° (Otto, *Zeitschr. f. Chem.* [2] vi. 25).

Mercuric Naphthylide. $Hg(C^{10}H^7)^2$ (Otto a. Möries, *Ann. Ch. Pharm.* cxlvii. 164; *Zeitschr. f. Chem.* [2] iii. 377; iv. 162; *Jahresb.* 1867, p. 715).—This compound is easily and abundantly formed by the action of sodium-amalgam on monobromonaphthalene:

$$2C^{10}H^7Br + Na^2Hg = Hg(C^{10}H^7)^2 + 2NaBr.$$

A solution of bromonaphthalene in several times its volume of coal-tar naphtha boiling between 120° and 140° is boiled for about nineteen hours with pasty sodium-amalgam, in a flask having an upright condenser, and the liquid is filtered hot, whereupon the mercuric naphthide crystallises out almost completely. After recrystallisation from benzol or carbon bisulphide, it forms small white crystals, appearing under the microscope as rhombic prisms terminated by four-sided pyramids. It is inodorous, unaffected by air and light, insoluble in water, slightly soluble in boiling alcohol, cold benzol, or ether, more easily in hot carbon bisulphide, chloroform, and benzol. It melts at 243° and decomposes at a higher temperature, depositing small quantities of charcoal and mercury, and yielding an oily crystallising distillate. By ignition with soda-lime it yields naphthalene, together with another hydrocarbon crystallising in canary-yellow laminæ, and melting at 133°. Heated with concentrated hydriodic, hydrobromic, or hydrochloric acid, it is resolved into naphthalene and mercuric iodide, bromide, or chloride. With iodine it unites directly, forming naphtho-mercuric di-iodide, $(C^{10}H^7)^2HgI^2$, which on further addition of iodine is resolved into mercuric iodide and iodonaphthalene, $C^{10}H^7I$.

Naphthomercuric Di-iodide, $(C^{10}H^7)^2HgI^2$ =  $Hg\left\langle\begin{matrix} I-C^{10}H^7 \\ | \\ I-C^{10}H^7 \end{matrix}\right.$ (the iodine being trivalent), is prepared by mixing the solutions of 1 mol. mercuric naphthylide and 1 mol. iodine in carbon bisulphide, distilling off the latter, and recrystallising the residue from hot alcohol. It forms soft satiny needles or dendritic groups, not altered by light, insoluble in water, slightly soluble in hot alcohol, chloroform, benzol, and carbon bisulphide, melting at 185°, and resolved by ignition with lime into naphthalene, iodine, and mercuric oxide.

Bromine acts on mercuric naphthylide in the same manner as iodine, forming in the first instance a crystallisable dibromide, which is decomposed by more bromine into bromonaphthalene and mercuric bromide.

Mercuric Acetoxynaphthlyide, $C^{12}H^{10}HgO^2 = Hg\left\{\begin{matrix} C^{10}H^7 \\ OC^2H^3O \end{matrix}\right.$, is produced, together with naphthalene, by heating mercuric naphthylide with excess of glacial acetic acid:

$$Hg(C^{10}H^7)^2 + HOC^2H^3O = C^{10}H^8 + Hg(C^{10}H^7)(OC^2H^3O).$$

On mixing the solution with a large quantity of hot water, and crystallising the resulting white precipitate from hot alcohol, naphthalene separates out, while mercuric acetoxynaphthylide remains in solution, and may be obtained by evaporation, prolonged heating, and recrystallisation. It is insoluble in water, easily soluble in hot glacial acetic acid, alcohol, carbon bisulphide, benzol, and chloroform, less soluble in ether; crystallises in small needles appearing under the microscope as flat rhombic prisms or tables; melts at 154°, and decomposes at a higher temperature, depositing charcoal, and yielding an oily distillate which quickly solidifies. With hydrochloric, hydriodic acid, &c., it reacts like mercuric naphthylide. It is not decomposed by heating with water to 140°, with ethyl iodide to 160°, or by sodium-amalgam, zinc, copper, or tin at ordinary temperatures; neither does it unite with mercuric chloride.

Mercuric Phenylide. $Hg(C^6H^5)^2$ (Dreher a. Otto, *Zeitschr. f. Chem.* [2] iv. 685; vi. 9).—This compound is prepared, like the naphthylide, by heating a mixture of monobromobenzene and anhydrous benzol (B. P. 100°–120°–140°) with pasty sodium-amalgam; the reaction may, however, be considerably facilitated by addition of a little acetic ether ($\frac{1}{10}$ of the weight of the bromobenzene).

Mercuric phenylide crystallises from a hot-saturated benzol-solution in small, white, vitreous, asbestos-like needles; from a dilute solution in white rhombic prisms often united in tufts. It is insoluble in water, easily soluble in chloroform, carbon bisulphide, and benzol, less easily in ether and boiling alcohol, slightly in cold alcohol. Melts at 120°; sublimes without decomposition when cautiously heated in small quantities; boils when heated above 300°, and distils, with formation of benzene and diphenyl, and separation of mercury and charcoal; probably thus:

$$3Hg(C^6H^5)^2 = 5C^6H^6 + Hg^3 + C^6$$

and

$$2C^6H^6 = C^{12}H^{10} + H^2.$$

It is quickly decomposed by dry *hydrochloric acid gas*, or by heating with the concentrated aqueous acid, into benzene and mercuric chloride:

$$Hg(C^6H^5)^2 + 2HCl = 2C^6H^6 + HgCl^2;$$

and reacts in a similar manner with hydriodic, hydrobromic, nitric, sulphuric acid, &c.

concentric or arborescent groups of silky crystals. The acid dissolves easily in alcohol and ether, and in 272·5 pts. of cold water, melts at 187·5° to 188°, and sublimes in small transparent needles. Neutral or slightly acid solutions form a red-brown precipitate with ferric chloride (R. Peltzer, *Ann. Ch. Pharm.* cxlvi. 284; *Zeitschr. f. Chem.* [2] v. 225).

Dibromo-paraoxybenzoic Acid. $C^7H^4Br^2O^3$.—The ethylic ether of this acid separates on adding saturated bromine-water to an alcohol solution of ethylic paraoxybenzoate diluted with hot water, in white flocks which separate from alcohol in short shining needles (Barth, *J. pr. Chem.* c. 366).

Iodoparaoxybenzoic acids are produced by the simultaneous action of iodine and iodic acid on paraoxybenzoic acid; the best proportions are those indicated by the following equation:

$$10C^7H^6O^3 + 3IO^3H + 6I^2 = 5C^7H^5IO^3 + 5C^7H^4I^2O^3 + 9H^2O.$$

The paraoxybenzoic acid is dissolved in hot water in a flask provided with an upright condenser; iodine and iodic acid are added in powder; and the liquid is heated nearly to boiling for about five minutes, and then quickly filtered. Di-iodoparabenzoic acid then remains on the filter, while the mono-iodated acid, contaminated with a small quantity of paraoxybenzoic acid separates from the filtrate. The mono-iodated acid is purified by repeated crystallisation from hot water, with addition of animal charcoal: it first separates in granules, but when nearly pure, in small needles having a glassy lustre (Peltzer, *loc. cit.*). It is also produced, though not in the pure state, by heating paraoxybenzoic acid with potassium iodate and sulphuric acid: the product is a resinous mass which when fused with potash is resolved into potassium iodide and protocatechuic acid (Barth; Peltzer).

Monoiodoparaoxybenzoic acid, in the air-dried state, contains $2C^7H^5IO^3 + H^2O$, and gives off its water at 100°. It dissolves in 576 pts. of cold water, much more easily in hot water, very easily in alcohol and ether. It melts at 160°, decomposes at 192° (iodosalicylic acid does not melt below 196°); when very gradually heated it sublimes, much below its melting point, in silky needles two lines long. The aqueous solution forms a dingy brown precipitate with ferric chloride. The *monosodic salt*, $C^6H^3I(OH).CO^2Na$, formed by adding the acid to a hot solution of sodium carbonate in sufficient quantity to produce strong acid reaction, removing the excess of acid by ether, and strongly concentrating the remaining solution, crystallises in fine efflorescent monoclinic crystals, often concentrically grouped. The *disodic salt*, $C^6H^3I(ONa).CO^2Na + 5H^2O$, is obtained by adding the acid to excess of hot aqueous sodium carbonate, adding a large quantity of alcohol, and evaporating the filtered solution to dryness. On redissolving in absolute alcohol and evaporating in a vacuum, the salt is obtained in hygroscopic silky needles, having a neutral reaction, and giving off their water at 130°. The *barium salt*, $(C^7H^4IO^3)^2Ba + 7H^2O$, forms transparent rhombic tables having their prismatic edges truncated; becomes anhydrous at 100°. The use of an excess of barium carbonate does not give rise to a salt richer in barium. The *silver salt*, $C^7H^4IO^3Ag$, is a white pulverulent precipitate nearly insoluble in water, easily soluble in ammonia (Peltzer).

Di-iodoparaoxybenzoic acid, $C^7H^4I^2O^3 = C^6H^2I^2(OH).CO^2H$, is easily purified by boiling it several times with water, dissolving the residue in sodium carbonate, precipitating with hydrochloric acid, then dissolving in strong alcohol, decolorising with animal charcoal, and mixing the solution with a sufficient quantity of water to produce turbidity; the acid is then deposited on cooling in small colourless needles. It is nearly insoluble in boiling water; dissolves easily in alcohol and ether; decomposes when heated, without previous fusion; and cannot be sublimed. Its two *sodium salts* are prepared similarly to those of the mono-iodated acid. The salt $C^7H^3I^2O^3Na + 7H^2O$ forms tufts of delicate, iridescent, efflorescent needles. The *disodic salt*, $C^7H^2I^2O^3Na^2 + 6H^2O$, forms transparent rhombic tables: both are easily soluble in water. From these salts two corresponding *silver salts* are obtained as flocculent curdy precipitates detonating when heated. The *barium salt*, $C^7H^2I^2O^3Ba$, is separated by alcohol from its aqueous solution, as a gelatinous precipitate, which dries up to a very loose white powder. The *calcium salt*, $C^7H^2I^2O^3Ca + 2H^2O$, crystallises from concentrated solution in nacreous laminæ, easily soluble in cold water. The *lead salt*, $C^7H^2I^2O^3Pb$, is formed, as a bulky precipitate, with elimination of acetic acid, when a solution of the disodic salt is mixed with lead acetate; when heated it swells up like mercuric sulphocyanate. Both mono- and di-iodoparaoxybenzoic acid are easily reduced by sodium-amalgam to para-oxybenzoic acid. The di-iodated acid is but imperfectly decomposed by fusion with sodium carbonate, even at 200°; the fused mass assumes a flesh-red colour on exposure to the air (Peltzer).

Iodo-methylparaoxybenzoic or *Iodanisic acid*, $C^8H^7IO^3 = C^6H^3I\left\{\begin{matrix}OCH^3\\CO^2H,\end{matrix}\right.$ is produced by heating 4 grms. of anisic acid to 145°–150° with the quantities of iodine and iodic acid corresponding to the equation:

$$5C^8H^8O^3 + IO^3H + 2I^2 = 3H^2O + 5C^8H^7IO^3.$$

The crystallised portion of the product contains, besides anisic acid, which may be extracted by boiling water, iodanisic acid and a non-acid body. The iodanisic acid is extracted by hot solution of sodium carbonate; the exactly neutralised solution precipitated by barium chloride; and the barium salt recrystallised from boiling water till the acid separated from it melts at 234·5°. The acid is nearly insoluble in boiling water, dissolves in 165 pts. of ether at ordinary temperatures, somewhat more easily in boiling ether and in alcohol, and crystallises from the two latter in needles having a vitreous lustre. Its ammonium salt crystallises in nodular groups of small needles; the *sodium salt*, $C^8H^6IO^3Na + 2H^2O$, in concentrically grouped needles; the *barium salt*, $(C^8H^6IO^3)^2Ba + 3H^2O$, in vitreous prisms; the *calcium salt*, $(C^8H^6IO^3)^2Ca + 3H^2O$, in nacreous laminæ. The *lead salt*, $(C^8H^6IO^3)^2Pb$, (at 100°) is a curdy precipitate, which cakes together on boiling. The *silver salt*, $C^8H^6IO^3Ag$, separates from boiling water in microcrystalline laminæ quickly blackened by light. The *copper* and *iron salts* are brown precipitates insoluble in water (Peltzer).

Nitroparaoxybenzoic and **Amidoparaoxybenzoic Acids** (Barth, *loc. cit.*).—The *dinitro-acid*, $C^7H^4(NO^2)^2O^3$, is obtained (but not quite free from the following compound) by dissolving paraoxybenzoic acid in warm nitric acid of sp. gr. 1·40, and crystallises from water in stellate groups of yellowish needles, which acquire a lemon-yellow colour on exposure to light and air. The *mononitro-acid*, $C^7H^5(NO^2)O^3$, which is more easily obtained pure, separates from a solution of paraoxybenzoic acid in 1 vol. nitric acid of 1·40 and 6 vol. water, in flesh-coloured crystals, which, after recrystallisation, exhibit sickle-shaped forms under the microscope. Both these nitro-acids, when treated with tin and hydrochloric acid, quickly yield double compounds of the hydrochlorides of the corresponding amido-acids with stannous chloride.

Ethylic Dinitroparaoxybenzoate is formed by dissolving ethylic paraoxybenzoate in strong nitric acid, and separates on cooling in radiate feathery crystals, and on addition of water as an oil which quickly crystallises in warty masses; after recrystallisation from alcohol it forms nearly colourless, very light needles, which become strongly electric by friction. *Ethylic mononitroparaoxybenzoate*, $C^7H^4(NO^2)O^3.C^2H^5$, is prepared by heating the paraoxybenzoic ether with 1 vol. nitric acid of sp. gr. 1·40 and 6 vol. water, till an oil separates which crystallises on cooling. Both these nitrated ethers melt below 100°, and solidify in the crystalline state on cooling.

The mononitrated ether reduced with tin and hydrochloric acid yields a yellow solution, which when freed from tin by hydrogen sulphide, deposits colourless laminæ of the *hydrochloride of ethyl amidoparaoxybenzoate*, $C^7H^4(NH^2)O^3(C^2H^5).HCl + \frac{1}{2}H^2O$. This compound in very dilute solution is coloured blood-red by ferric chloride, and is therefore only isomeric with tyrosine hydrochloride, which does not exhibit this reaction. (See TYROSINE.) *Ethyl amidoparaoxybenzoate* cannot be separated from this compound, on account of its instability. The mother-liquor of the hydrochloride, especially if mixed with hydrochloric acid, deposits crystals of the *hydrochloride of amidoparaoxybenzoic acid*. This last-mentioned compound mixed in moderately dilute solution with sulphuric acid, solidifies to a crystalline pulp consisting of the *sulphate of amidoparaoxybenzoic acid*, which when treated with cold concentrated nitric acid, acquires a splendid dark cherry-red colour. *Amidoparaoxybenzoic acid*, $C^7H^5(NH^2)O^3 + \frac{1}{2}H^2O$, prepared by decomposing the sulphate with baryta-water, neutralising the filtrate with lead carbonate, and decomposing the resulting lead salt with hydrogen sulphide, crystallises in needles, which decompose even below 100°, and appear under the microscope as hexagonal scalenohedrons, often with curved faces (Barth).

PARATOLUIDINE. See TOLUIDINE.

PARTZITE. A silver ore discovered by A. W. Partz in the Blind Spring mountains, Mono County, California. It forms dull amorphous masses having a conchoïdal to uneven fracture, and yellowish-green, blackish-green, or black colour. Hardness between 3 and 4. Sp. gr. = 3·8. Contains 47·65 p. c. Sb^2O^3, 32·11 CuO, 6·12 Ag^2O, 2·01 PbO, 2·33 FeO, and 8·29 water (= 98·51), agreeing with the formula $(CuO ; Ag^2O ; PbO ; FeO)Sb^2O^3 + 3H^2O$ (Arents, *Sill. Am. J.* [2] xliii. 362).

PASTREITE. A yellow amorphous ferric sulphate, found, together with cerusite and fibroferrite, at Paillières, near Alais, in the Dép. du Gard, on the rubbish-heaps of mines from which argentiferous galena and iron pyrites are obtained. Contains 30·47 p. c. SO^3, 46·50 Fe^2O^3, and 16·04 water, together with 1·86 As^2O^3, 2·40 SiO^2, 1·25 PbO, and 0·89 lime, clay, and manganese (Bergemann, *Jahresb.* 1867, p. 1005).

PATELLARIC ACID. $C^7H^{20}O^{10}$.—This acid, obtained some time ago by Knop, from the lichen *Parmelia scruposa* or *Patellaria scruposa*, has been further examined by Weigelt (*Zeitschr. f. Chem.* [2] v. 298). It does not appear to be identical with any of the known lichen acids. It unites easily with bases, and yields with cold baryta-water a salt having a transient blue colour. Boiling baryta-water decomposes it, forming carbonate and oxalate of barium, together with a barium salt of a new acid (*β patellaric acid*) possessing, to a certain extent, essentially different qualities. Patellaric acid forms two series of salts, in which 1 and 2 at. H are replaced by metals. The formation of the salt $C^{17}H^{18}(NH^4)^2O^{10}$ appears to require the aid of sunshine. Among the decomposition-products of the acid are carbonic acid, oxalic acid, and orcin. The lichen contains between 2 and 3 per cent. of patellaric acid. The acid is situated between the layers of the outer bark and the gonidia, where it was detected microscopically by the reaction with baryta-water.

PATSCHOULI. Volatile oil of patschouli gradually deposits a camphor or stearoptene, the formation of which may be accelerated by dehydrating the oil with calcium chloride. This camphor is homologous with that of Borneo, and has the composition $C^{15}H^{28}O$; vapour-density obs. = 8·00; calc. = 7·85. It melts at 54°–55°, boils at 296°, and has a sp. gr. of 1·051 at 4·5°. It is insoluble in water, easily soluble in alcohol and ether, and separates from these solutions by slow evaporation, sometimes in large and very well-defined hexagonal prisms terminated by six-sided pyramids. The alcoholic solution is lævogyrate, a solution of 1 grm. in 5·3 c. c. alcohol in a tube 0·05 met. long producing a deflection of 9·1°. The camphor distilled over zinc chloride yields a hydrocarbon, $C^{15}H^{26}$, which boils at 248°–252°, and appears to be converted into polymeric hydrocarbons at slightly higher temperatures. The oil from which the camphor has been deposited passes over almost entirely between 282° and 294°, has the same composition as the camphor, and yields the same hydrocarbon when treated with zinc chloride. It is also lævogyrate, but less so than the camphor, producing under the conditions above mentioned, a deflection of only 3° (H. Gal, *Compt. rend.* lxviii. 406).

PECTOLITE. The mineral from Niederkirchen, near Wolfstein in the Rheinpfalz, called *osmelite* by Breithaupt, appears, from a renewed examination by v. Kobell (*J. pr. Chem.* xcvii. 493; *Jahresb.* 1866, p. 935), to have the composition and all the properties of pectolite. It is intergrown with a brown friable mineral, very similar to it in structure, which appears to have been formed from it by the action of water and carbonic acid.

PECTOUS SUBSTANCES (iv. 363). On the preparation of pectin from turnips, see Stüde (*Ann. Ch. Pharm.* cxxxi. 244; *Jahresb.* 1864, p. 587).*

On the preparation of metapectic acid from horse-chestnut bark, see Rochleder (*Zeitschr. f. Chem.* [2] iv. 381). Metapectic acid heated with excess of potassium hydrate is resolved into formic and protocatechuic acids:

$$C^8H^{10}O^7 = CH^2O^2 + C^7H^6O^4 + H^2O.$$

The formation of pyropectic acid, $C^{14}H^{18}O^9$, from metapectic acid, by the action of heat, is represented by the equation: $2C^8H^{10}O^7 = C^{14}H^{18}O^9 + 2CO^2 + H^2O$ (Rochleder).

Scheibler (*Deut. chem. Ges. Ber.* 1868, pp. 58, 108; *Zeitschr. f. Chem.* iv. 433) prepares metapectic acid by heating turnip-pulp with milk of lime on the water-bath, decomposing the resulting calcium salt with ammonium carbonate, precipitating the ammoniacal solution with basic lead acetate, separating the acid by hydrogen sulphide (removing the last portions of lead, if necessary, by sulphuric acid), and decolorising it with animal charcoal free from lime. The acid thus prepared possesses all the properties of that described by Frémy (iv. 369), excepting that its alkali-metal salts are not precipitated by basic or neutral lead acetate in neutral solution, but only on addition of ammonia; and that, instead of being optically inactive, it exhibits a very strong lævogyration, 1 pt. of it being sufficient to neutralise the dextrogyrate power of 1½ pt. dextroglucose. This lævogyrate power is not altered by saturating or supersaturating the solution of the acid with alkalis or alkaline earths; but on boiling the solution with a strong acid, mineral or organic, it quickly diminishes, becomes nothing, and then passes into dextrogyration, ultimately equal in magnitude to the original lævogyration. This change arises from the resolution of the metapectic acid into an organic acid precipitable by lead acetate, and a dextrogyrate sugar, pectin-sugar: metapectic acid is therefore a glucoside.

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* See also vol. iv. p. 364, in which (line 9 from bottom) read 'turnips' instead of 'radishes.'

Pectin-sugar, $C^6H^{12}O^6$, crystallises in long brittle prisms with dihedral summits. It is less sweet than cane-sugar, dissolves easily in boiling water, and separates therefrom on cooling. At 160° it melts to a transparent liquid, which solidifies to a crystalline mass on cooling; at higher temperatures it carbonises, and gives off an acid distillate. It is carbonised by sulphuric acid, and when treated with nitric acid yields oxalic but no mucic acid. Alkalis and alkaline earths are dissolved by it, and quickly turn it brown when heated with it; the lime-solution is precipitated by alcohol. Its dextrogyrate power exceeds that of all other kinds of sugar except trehalose and lactose, and is 1·6 time as great as that of dextroglucose; $[\alpha] = +118°$ for the transition tint. Pectin-sugar very easily reduces an alkaline solution of potassio-cupric tartrate (Fehling's solution). From an ammoniacal silver solution at 100° it throws down a speculum of silver. It is not brought into alcoholic fermentation by yeast (Scheibler).

PELARGONIC ACID. $C^9H^{18}O^2$.—The compound of this acid with nitrogen dioxide, $C^9H^{18}O^2.N^2O^3$, which Chiozza obtained as a secondary product in the preparation of pelargonic acid by the action of nitric acid on oil of rue (*Compt. rend.* xxxv. 797; *Jahresb.* 1852, p. 499), may be prepared, according to Alexeyeff (*Zeitschr. f. Chem.* [2] i. 736), by heating oil of rue with an equal volume of nitric acid of sp. gr. 1·2. When the action is complete, the oil which separates is washed with water and treated with potash. The liquid diluted with water deposits an abundant precipitate of the potassium salt of nitroso-pelargonic acid, which may be purified by recrystallisation from boiling water. The barium salt obtained by double decomposition has, according to Chiozza, the composition $(C^9H^{17}O^2.N^2O^3)^2Ba$. The silver salt of analogous constitution burns with a greenish flame. The acid separated from its potassium salt is an oily liquid, which when heated suddenly gives off large quantities of nitrogen dioxide mixed with combustible gases (Chiozza).

PELARGONITRILE, $C^9H^{17}N$, or **OCTYL CYANIDE,** $C^8H^{17}.CN$.—See CYANIDES, ALCOHOLIC (p. 525).

PENNINE. Fellenberg (*Jahresb.* 1867, p. 992) found for pennine: A from Rimfischgrat, B from Zermatt, the following percentage composition, whence he deduces for A the formula $5(4MgO.3SiO^2) + 2(3MgO.Al^2O^3) + 20H^2O$; for B the formula $3(4MgO.3SiO^2) + 2(2MgO.Al^2O^3) + 12H^2O$:

SiO^2	Al^2O^3	Cr^2O^3	Fe^2O^3	FeO	MgO	H^2O	
33·12	13·25	0·60	1·52	4·69	34·04	12·87	= 100·09
33·97	11·66	—	2·49	1·81	37·60	13·57	= 101·10

PENTADECANE. $C^{15}H^{32}$. *Benyl Hydride.*—This hydrocarbon, obtained from American petroleum, has a sp. gr. of 0·825 at 19°, and boils at 258° to 262°. With chlorine it yields pentadecyl chloride, $C^{15}H^{31}Cl$ (Pelouze a. Cahours). When passed through red-hot tubes, it is for the most part converted into decane, $C^{10}H^{22}$ (Vohl, *Jahresb.* 1865, p. 841).

PENTADECINE. $C^{15}H^{28}$. *Benylene.*—This hydrocarbon, homologous with ethine or acetylene, and related to benic acid, $C^{15}H^{30}O^2$, in the same manner as quintine or valerylene to valeric acid, is produced by heating triamylene acetate with potash:

$$C^{15}H^{30}.(C^2H^3O^2)^2 + 2KHO = 2C^2H^3O^2K + 2H^2O + C^{15}H^{28}.$$

It is a thickish, colourless, faintly smelling liquid, boiling at 230°–240°. It unites with bromine, producing great rise of temperature, and, if well cooled, without perceptible evolution of hydrobromic acid (Bauer, *Ann. Ch. Pharm.* cxxxvii. 249).

PENTAHIROLINE. $C^{13}H^{15}N$.—A homologue of chinoline occurring among the higher products of the dry distillation of cinchonine (C. Gr. Williams, *Laboratory*, i. 109).

PERIDOTE. Lechartier (*Compt. rend.* lxvii. 41; *Zeitschr. f. Chem.* [2] iv. 606) prepares peridotes and pyroxenes by mixing the required oxides with silica, introducing the mixture, together with anhydrous calcium chloride, into a graphite crucible contained within an earthen crucible, the intervening space being packed with charcoal powder, and igniting the mixture strongly for an hour or two. The fused mass when treated with water leaves the silicate in the crystalline form. For silicates containing iron and manganese, a clay crucible is used instead of the graphite crucible, and the and decomposes at a higher temperature. It unites with hydrochloric acid, forming the compound $C^9H^9(NH^2)O^2.HCl$, which crystallises from excess of hydrochloric acid in long needles, and is decomposed by heating its aqueous solution, with separation of free amidomesitylenic acid.

Mesitylenamide, $C^9H^9O.NH^2$, is obtained by gently heating 1 mol. mesitylenic acid with rather more than 1 mol. phosphorus pentachloride, adding the product to strong aqueous ammonia, washing the resulting crystalline pulp with dilute ammonia, and recrystallising from boiling water. It crystallises in long needles; melts at 133°; sublimes without decomposition; dissolves sparingly in cold, more easily in boiling water, also in alcohol and ether; and is decomposed by alkalis into ammonia and mesitylenate.

Oxymesitylenic acid, $C^9H^{10}O^3 = C^6H^2\left\{\begin{matrix}OH\\(CH^3)^2\\CO^2H\end{matrix}\right.$, is produced by heating the dry potassium salt of mesitylene-sulphuric acid with three times its weight of potassium hydrate to 240°–250°:

$$C^6H^2\left\{\begin{matrix}SO^2KO\\(CH^3)^2\end{matrix}\right. + 3KHO = C^6H^2\left\{\begin{matrix}OK\\(CH^3)^2\\CO^2K\end{matrix}\right. + K^2SO^3 + 3H.$$

Potassium mesitylene-sulphate. Dipotassic Oxymesitylenate.

Part of the oxymesitylenate is at the same time converted into the potassium-compound of isoxylylic phenol, $C^6H^4(CH^3)^2O$, which is moreover the chief product obtained when the temperature is raised to 280°:

$$C^6H^2\left\{\begin{matrix}OK\\(CH^3)^2\\CO^2K\end{matrix}\right. + KHO = C^6H^3\left\{\begin{matrix}OK\\(CH^3)^2\end{matrix}\right. + K^2CO^3.$$

On dissolving the cooled mass in water, acidulating with sulphuric acid, and distilling, a small quantity of isoxylylic phenol passes over at first with the vapour of water; and if the distillation be continued as long as suddenly solidifying oil-drops appear in the condensing tube, the residual liquid repeatedly agitated with ether, and the ether evaporated, oxymesitylenic acid is obtained as a dark-coloured crystalline mass. It may be purified by repeated solution in sodium carbonate, precipitation with hydrochloric acid, conversion into barium salt, repeated crystallisation of this salt from water, separation of the acid therefrom by hydrochloric acid, repeated crystallisation from alcohol, and final sublimation.

Oxymesitylenic acid melts at 176°; sublimes without decomposition in broad dazzling white needles nearly an inch long, insoluble in cold, slightly soluble in hot water, very soluble in alcohol and ether; and crystallises from dilute alcohol in long silky needles. The aqueous solution of the acid or its salts acquires, on addition of a drop of ferric chloride, a very deep blue colour with a faint tinge of violet, changing to dirty yellow at the boiling heat. Free acids and alkalis interfere with this reaction. *Barium oxymesitylenate*, $(C^9H^9O^3)^2Ba + 5H^2O$, forms compact groups of hard shining laminæ, very soluble in hot, moderately soluble in cold water, turning brown at 110° and black at 130°. The *calcium salt*, $(C^9H^9O^3)^2Ca + 5H^2O$, crystallises in dense tufts of colourless needles easily soluble in water, especially at the boiling heat, somewhat more permanent than the barium salt (Fittig a. Hoogewerff).

MESOSIDERITE. This name is applied by G. Rose to meteorites consisting of nearly equal portions of metal and silicates (*Beschreibung und Eintheilung der Meteoriten*, Berlin, 1864; *Jahresb.* 1863, p. 909; 1865, p. 945).

MESOXALIC ACID. $C^3H^2O^5$.—This acid, originally obtained, together with urea, by boiling alloxan or alloxanic acid with alkalis (iii. 932), is also produced by oxidation of amidomalonic acid, *e.g.* by treating that acid with iodine and water (iv. 115):

$$C^3H^3(NH^2)O^4 + H^2O + I^2 = C^3H^2O^5 + HI + NH^4I.$$

On the preparation of mesoxalic acid from alloxan, see Deichsel (*Berl. Akad. Ber.* 1864, p. 587; *Jahresb.* 1864, p. 640). It crystallises from a syrupy solution evaporated at 40°–50°, and finally over sulphuric acid, in prismatic crystals, $C^3H^2O^5.H^2O$, very deliquescent, easily soluble in alcohol, melting without loss of water at 115°, and resolidifying at 55°. It has a strong acid taste and reaction; decomposes in concentrated aqueous solution at 70°–80°; forms with barium and lead acetate, flocculent precipitates which gradually become crystalline; and after neutralisation with ammonia, is precipitated by barium and calcium salts, also by silver

With a smaller quantity of water (6 to 10 pts.) dibromosuccinic acid is obtained, together with bromoform, hydrobromic acid, and carbon dioxide:

$$C^6H^6O^6 + 3Br^2 = C^4H^4Br^2O^4 + CHBr^3 + CO^2 + HBr.$$

When the product of this last reaction is boiled with baryta-water, the dibromosuccinic acid is converted into paratartaric acid, identical in crystalline form and most of its properties with natural racemic acid:

$$C^4H^4Br^2O^4 + 2H^2O = 2HBr + C^4H^6O^6.$$

Phenaconic acid is a strong acid containing 4 atoms of replaceable hydrogen. Its salts crystallise well, and are mostly composed according to the general formula: $C^6H^3O^6R^3$. With the alkali-metals it likewise forms salts containing 2 or 1 at. metal, but not double salts containing the alkali-metals together with other metals. These salts give off their water of crystallisation between 100° and 150°, and decompose at higher temperatures, leaving more or less charcoal, and giving off acid vapours smelling like acetic acid, without a trace of products containing less hydrogen. Free phenaconic acid is not precipitated by any of the ordinary reagents; the solutions of its ammonium and barium salts give with ferric chloride a brownish-yellow pulverulent precipitate; with cupric acetate no precipitate in the cold, but at the boiling heat green gelatinous flocks which redissolve on cooling. Silver nitrate and lead acetate slowly added to the solution, produce transient turbidity, and the liquid if then left at rest, deposits crystalline phenaconate of silver or lead; by an excess of the precipitant these salts are thrown down in the amorphous state.

The *potassium salts*, $C^6H^3O^6K^3$, $C^6H^3O^6K^2H$, and $C^6H^3O^6KH^2$, obtained by precipitating the barium salt with potassium sulphate, or partially with sulphuric acid, form hydrated easily soluble crystals. An *acid ammonium salt* remains on evaporating a solution of the acid neutralised with ammonia; an *ammonio-potassic salt*, $C^6H^4O^6K(NH^4) + H^2O$, is obtained in like manner by saturating the dipotassic salt with ammonia and evaporating. The *calcium salt*, $(C^6H^3O^6)^2Ca^3 + 4H^2O$, forms nacreous tables and laminæ like those of the oxalate; it is soluble in alcohol, and on rapid evaporation crystallises with 8 mol. water. The *barium salt*, $(C^6H^3O^6)^2Ba^3 + 4H^2O$, crystallises in tables and laminæ, sometimes also in prisms; dissolves slowly in cold water (100 pts. water at 17° dissolve 0·9663 pt.); more quickly but not more abundantly in hot water. The *copper salt*, $C^6H^3O^6Cu^3 + 4H^2O$, separates on evaporating a solution of the acid saturated with cupric oxide, as a greenish indistinctly crystalline powder. The same salt is obtained in beautiful blue monoclinic tables on evaporating a solution containing the constituents of the soluble salt, $(C^6H^3O^6)^2Cu^2K^2$. The *lead salt*, $(C^6H^3O^6)^2Pb^3$ (at 120°), prepared as above described, crystallises in oblique rhombic tables and prisms. The *silver salt* forms microscopic tables and prisms, giving off water at 90°, and blackening both when heated in the dry state and when boiled with water (whereby it is abundantly dissolved); it is easily soluble in acetic and in phenaconic acid. With ethyl iodide it forms neutral *ethyl phenaconate*, $C^6H^3O^6.(C^2H^5)^3$, as an oily liquid having a faint odour, and distilling without decomposition. The same ether is formed by treating phenaconic chloride with alcohol; it is heavier than water, insoluble therein, and boils at 225°.

Phenaconic Chloride, $C^6H^3O^3.Cl^3$, produced by the action of phosphorus pentachloride on the acid, is a colourless liquid boiling at 165°, and decomposing at 250°; it sinks in water and is immediately decomposed thereby, reproducing phenaconic acid. Vapour-density obs. 7·62 and 7·60; calc. = 7·952.

PHENETOL-SULPHURIC ACID. $C^6H^4\left\{\begin{matrix}OC^2H^5\\SO^3H\end{matrix}\right.$.—When phenetol (ethylphenol) is heated with an equal weight of strong sulphuric acid, the resulting crystalline mass dissolved in water, and the solution neutralised with baryta, a barium salt, $(C^6H^4.OC^2H^5.SO^3)^2Ba + 4H^2O$, separates in tabular and lancet-shaped crystals, nearly insoluble in cold, slightly soluble in hot water. The mother-liquor retains a very soluble barium salt of an isomeric acid, distinguished as *phenetolparasulphuric acid*, the salts of which are all amorphous, and therefore not well characterised. *Lead phenetolsulphate*, $(C^6H^4.OC^2H^5.SO^3)^2Pb$, obtained by neutralising the acid with lead carbonate, crystallises from the concentrated solution in cauliflower-like masses, the phenetolparasulphate remaining in solution. *Potassium phenetolsulphate*, $C^6H^4.OC^2H^5.SO^3K + H^2O$, crystallises in large silky needles easily soluble in cold water, slightly soluble in boiling alcohol. The *silver salt* is completely decomposed by evaporation, with separation of silver (Opl a. Lippmann, *Compt. rend.* lxviii. 1332).

PHENOL. $C^6H^6O = C^6H^5OH$. *Phenyl Hydrate. Phenyl Alcohol.*—This compound is formed: 1. By heating anisol with concentrated hydriodic or hydrochloric acid to 130°–140° (Graebe, *Ann. Ch. Pharm.* cxxxix. 149):

$$C^6H^5OCH^3 + HI = CH^3I + C^6H^5OH.$$

2. By boiling the sulphate, nitrate, or hydrobromide of diazobenzene with water (Griess, *ibid.* cxxxvii. 39):

$$C^6H^4N^2.SO^4H^2 + H^2O = SO^4H^2 + N^2 + C^6H^6O.$$

3. By fusing potassium phenylsulphite with excess of potash (Wurtz, *Bull. Soc. Chim.* [2] viii. 197):

$$C^6H^5.SO^3K + KOH = SO^3K^2 + C^6H^5OH.$$

4. By heating acetylene with fuming sulphuric acid, whereby it is converted into the acid $C^2H^2SO^4$, and fusing the potassium salt of this acid with potash. The acetylene is then separated and polymerised, and the polymeric compound takes up oxygen, $3C^2H^2 + O = C^6H^6O$ (Berthelot, *Compt. rend.* lxviii. 539).

The phenol obtained by distilling oxybenzoic acid with lime (iv. 205) is identical with that produced in like manner from parabenzoic and salicylic acids, and with that obtained from coal-tar (Rosenthal, *Zeitschr. f. Chem.* [2] v. 627).

Preparation.—The following method of obtaining pure phenol from coal-tar is given by Hugo Müller (*Zeitschr. f. Chem.* [2] i. 270). The aqueous solution obtained by treating coal-tar with caustic soda or milk of lime, or a mixture of the two—which contains, besides phenol, certain easily oxidisable substances, and a not inconsiderable quantity of naphthalene—is diluted with water as long as naphthalene is thereby separated, and the liquid, which soon turns dark brown, is exposed to the air in shallow vessels for several days and frequently stirred. The brown solution is then filtered, the quantity of phenol contained in a given quantity of it is determined; and the quantity of acid required to precipitate the entire amount is calculated therefrom. If now ⅙ to ⅛ of this quantity of acid be added to the liquid with constant stirring, the resinous substances altered by the action of the air are first precipitated, together with larger or smaller quantities of cresol and xylol. A further addition of acid precipitates chiefly cresol, and after a few trials it is generally possible so to adjust the quantity of acid that the third and last precipitation shall yield nearly pure phenol, which crystallises after a single distillation. As even a small quantity of water prevents the crystallisation of phenol, it is necessary to remove this water completely by heating the phenol nearly to the boiling point, while a stream of dry air is passed over it. The crystallisation may be accelerated by cooling, or by the introduction of a small quantity of crystallised phenol. Crude phenol, such as is obtained from tar-refineries, may be conveniently purified by treating it several times in succession with soda-ley. The first extracts contain the purer product: the precipitation of the phenol must however be preceded by dilution with water and exposure to the air. A perfectly pure product, remaining colourless when preserved, is obtained only when the substances which turn brown by oxidation have been completely removed by exposure to the air. Phenol commonly contains a small quantity of a very disagreeably smelling sulphur-compound (phenyl sulphide), which may be removed by distillation over a small quantity of lead oxide.

For the preparation of crystallised phenol, Bickerdike (*Chem. News*, xvi. 188) recommends that the commercial product purified by one rectification be dehydrated with 1 or 2 p. c. of anhydrous cupric sulphate. The distillate solidifies for the most part at 16°, especially in contact with solid phenol.

Reactions.—1. An alcoholic solution of phenol is turned brown by an alcoholic solution of *ferric chloride*; wood-tar creosote similarly treated yields a solution of a fine emerald-green colour (Frisch, *J. pr. Chem.* c. 223:—Gorup-Besanez, *Ann. Ch. Pharm.* cxliii. 129).—2. When a few sticks of potash are immersed in a solution of phenol in chloroform, the potash becomes covered with a rose-coloured layer which gradually dissolves, the liquid becoming very hot and ultimately brown and viscid. The first product is a brown amorphous mass, soluble in alkalis, reprecipitated by acids, and apparently consisting of two substances, one of which dissolves very easily in alkaline carbonates, less easily in strong sulphuric acid; this latter solution gives with water, a precipitate exhibiting with alkalis the reactions of rosolic acid. The other substance is less soluble in alkalis, but dissolves very easily in strong sulphuric acid, and is not reprecipitated by water. If carbon tetrachloride be used as the solvent instead of chloroform, no reaction takes place in the cold, but at 180° the liquid assumes the colour of rosolic acid. When wood-tar creosote is treated in the same manner, a very similar reaction takes place, but the product is altogether different, forming with sulphuric acid a deep crimson solution, from which water throws down a green precipitate. Moreover, the products obtained as above from phenol colour silk and wool brown in alkaline solution, whereas those from creosote exhibit no tinctorial power (C. Crump, *Chem. News*, xx. 126).

3. *Potassium permanganate* is immediately decolorised by aqueous phenol, and if the permanganate be added till the colour no longer disappears, the only products are carbonic and oxalic acids; by incomplete oxidation there is formed—besides a resin very near to phenol in composition—only oxalic acid in determinable quantity, together with extremely small quantities of resinous and syrupy bodies (Tollens, *Zeitschr. f. Chem.* [2] iv. 715).

4. Phenol-vapour passed over heated *zinc-dust* is easily reduced to benzene, together with small quantities of liquid and solid secondary products of higher boiling point.

5. Phenol heated with *carbon dioxide* under strong pressure yields crystals resembling rock-salt, of a compound probably containing $3C^6H^6O.CO^2$ (Barth, *Ann. Ch. Pharm.* cxlviii. 49).

6. Phenol dissolves easily in an equal weight of strong *sulphuric acid*, producing two isomeric acids, $C^6H^4(OH).SO^3H$, distinguished as phenyl-parasulphuric and phenyl-metasulphuric acid (Kekulé, *Zeitschr. f. Chem.* [2] iii. 197) (see p. 923). When 2 pts. of crystallised phenol and 3 pts. hydrogen sulphate are heated for three or four hours to 160°, and the viscid product is poured into cold water, crystals of oxysulphobenzide, $C^{12}H^{10}SO^4$ (p. 894), are deposited (Glutz, *Ann. Ch. Pharm.* cxlvii. 52).

7. Phenol heated to 150° for three or four hours in sealed tubes with *sulphuryl chloride* is converted chiefly into monochlorophenol (Dubois, *Zeitschr. f. Chem.* [2] ii. 705):

$$C^6H^6O + SO^2Cl^2 = HCl + SO^2 + C^6H^5ClO.$$

8. According to Glutz (*Ann. Ch. Pharm.* cxliii. 180), a mixture of equal parts of phenol and *phosphorus pentachloride* heated to 100° for about three hours, and then distilled over the open fire, yields a large quantity of chlorobenzene or phenyl chloride, C^6H^5Cl. No phosphorus oxychloride is obtained, because it reacts with the phenol in such a manner as to form triphenylic phosphate:

$$3C^6H^6O + POCl^3 = 3HCl + PO^4(C^6H^5)^3.$$

Otto (*ibid.* cxlvii. 317) obtained by the same process only a very small quantity of phenyl chloride (compare iv. 390).

9. On adding *phosphoric anhydride* to pure liquefied phenol, a viscid syrup is formed, which, after standing for 24 hours at 40°, contains mono- and di-phenylic phosphate (Rembold, *Zeitschr. f. Chem.* [2] ii. 651).—10. Phenol distilled with pulverised *phosphorus pentasulphide* yields phenyl sulphydrate, C^6H^5SH, and phenyl sulphide, $(C^6H^5)^2S$ (Kekulé a. Szuch, *Compt. rend.* lxiv. 752).

On the constitution of the compounds of phenol with bases, see Romei (*Bull. Soc. Chim.* [2] xi. 120; *Zeitschr. f. Chem.* [2] v. 383).

Bromophenols (Körner, *Ann. Ch. Pharm.* cxxxvii. 197).—*Monobromophenol*, C^6H^4BrOH, originally obtained by Cahours by distilling bromosalicylic acid with baryta, is also produced when air saturated with the vapour of 160 pts. bromine is passed into 94 pts. of cooled phenol (on passing the hydrobromic acid thereby evolved into water, the solution deposits after a while flocks and threads of nearly pure tribromophenol). The still impure monobromophenol remaining in the flask is washed with dilute soda-ley, reprecipitated by dilute hydrochloric acid, and the separated oil, after washing with water, is distilled under reduced pressure. The same compound may be prepared more quickly, though with greater loss, by carefully mixing a cooled solution of phenol in 6 to 8 pts. carbon bisulphide with bromine, and after removal of the solvent, purifying the product by distillation as above.

Monobromophenol is a colourless oily liquid, of sp. gr. 1·6606 at 30°, and boiling at 132° under a pressure of 22 mm., or at 118° under a pressure of 9 mm. It does not solidify at −18°; is very easily coloured brown by dust, &c.; has an unpleasantly penetrating odour; instantly produces a white blister on the skin; is insoluble in water, but dissolves in all proportions of alcohol, ether, benzol, and carbon bisulphide. It unites with alkalis, forming salts which are very soluble in water. Heated with alcoholic potash to 160°–180° it forms potassium rosolate, and with a large excess of potash, also phenol. Heated with 1 mol. sodium hydrate and methyl iodide to 100°–120°, it is converted into *methylic monobromophenate*, $C^6H^4BrO.CH^3$, a colourless mobile liquid having an ethereal odour, a burning aromatic taste, and boiling at 223° (corr.).

Dibromophenol, $C^6H^3Br^2OH$, is prepared in the same manner as monobromophenol, using the requisite quantities of the materials, and collecting apart the portion which distils at 154° under a pressure of 11 mm. It forms a crystalline mass having a satiny lustre and unpleasant odour, melting at 40°, and subliming even at ordinary temperatures. It distils quite undecomposed under reduced pressure, and for the most part also under the ordinary pressure; is nearly insoluble in water, but dissolves easily in alcohol, ether, benzol, and carbon bisulphide. By nitric acid it is easily converted into picric acid. Its potassium salt forms white deliquescent nodules. *Methylic dibromophenate*, produced by heating dibromophenol to 100°–120° with caustic soda and methyl iodide, is identical with that which Cahours obtained by the action of bromine on anisol. It melts at 59°, boils at 272°, and crystallises from alcohol in nacreous scales, after fusion and partial cooling in large highly lustrous tables.

Tribromophenol, $C^6H^2Br^3.OH$, is easily formed by dropping bromine into phenol cooled at first, but afterwards gently warmed, as a crystalline mass, which when recrystallised from hot alcohol with addition of a little water, forms long silky needles, melting at 95°, easily subliming, nearly insoluble in water, easily soluble in alcohol, and uniting with bases to form salts, some of which crystallise well.

Tetrabromophenol, C^6HBr^4OH, is produced by heating pure tribromophenol with 1 mol. bromine to 170°–180°, and after repeated crystallisation and sublimation of the portion of medium solubility, forms concentric needles which melt at 120°, and dissolve very easily in alcohol.

Pentabromophenol, C^6Br^5OH, is obtained by heating tetra- or tri- bromophenol with excess of bromine to 210°–220° for several days, washing the product with water, and recrystallising it from carbon bisulphide. It dissolves but slowly in alcohol or carbon bisulphide, and crystallises from the latter in large adamantine needles, from the former in concentrically grouped needles, which melt at 225°, and sublime without decomposition when cautiously heated. With strong nitric acid it forms bromopicrin and bromanil, $C^6Br^4O^2$ (Körner).

Chlorophenols. *Monochlorophenol*, C^6H^4ClOH, is prepared: 1. By slowly passing chlorine into well-cooled phenol (500 grms.), distilling after about twelve hours, collecting apart the portion which goes over between 215° and 225°, and rectifying.—2. By the action of sulphuryl chloride on phenol (p. 907). It is a white crystalline body having a penetrating odour, melting at 41°, boiling at about 220°, soluble in alcohol, ether, benzol, and aqueous caustic alkalis, but not in alkaline carbonates (Dubois, *Zeitschr. f. Chem.* [2] iii. 205). Bähr-Predari (*ibid.* vi. 246), by passing chlorine into phenol mixed with a little water and cooled with ice, washing the product with weak potash-solution, dehydrating with calcium chloride and anhydrous cupric sulphate, then filtering and fractionating, has obtained a monochlorophenol melting at 8·5° and boiling at 220°. Heated with potash to 190°, it appears to yield hydroquinone.

Dichlorophenol, $C^6H^3Cl^2.OH$, previously known only as an oil (iv. 392), is obtained by passing dry chlorine into phenol, repeated fractional distillation, and recrystallisation from benzol, in colourless slender six-sided needles several inches long, exhibiting a pale reddish tint when dried and viewed in mass. It melts at 42°–43°, boils at 209°, and does not therefore appear to correspond with monochlorophenol (which boils at 220°). It is nearly insoluble in water, but dissolves very easily in alcohol, ether, and warm benzol. It has an unpleasant odour, volatilises with vapour of water, and expels carbonic acid from alkaline and earthy carbonates when boiled with them in presence of water; in the cold, however, it is separated from these solutions by carbonic acid. Its *ammonium salt*, $C^6H^3Cl^2O(NH^4)$, crystallises from a hot solution of dichlorophenol in strong ammonia, in colourless shining needles; from dilute solutions in tables apparently rhombic. The *potassium salt* forms thin colourless rhombic tables, quickly becoming greyish-violet on exposure to light, especially when moist, easily soluble in water and alcohol, giving off the free acid even at 70°. The *silver salt* is a yellowish amorphous precipitate, quickly blackening, even in the dark. The *lead salt* (probably basic $C^6H^3Cl^2O.Pb.OH$), precipitated from the solution of the ammonium salt, is white and amorphous. The *ethylic ether*, $C^6H^3Cl^2OC^2H^5$, obtained by boiling the potassium salt with ethyl iodide, precipitating with water and rectifying, is a colourless oil boiling at 226°–227°, nearly insoluble in water, miscible in all proportions with alcohol and ether (F. Fischer, *Zeitschr. f. Chem.* [2] iv. 386).

Another modification of dichlorophenol is obtained by passing nitrous acid vapour into a cooled mixture, of dichlor-orthoamidophenol sulphate (p. 913) and dilute sulphuric acid, whereby diazodichlorophenol sulphate is separated as a light brown crystalline powder; heating this powder with water and sodium carbonate; and distilling the product with sulphuric acid. Dichlorophenol then separates from the distillate in slender colourless needles (sometimes also as a faintly yellow oil) very slightly soluble in water, miscible in all proportions with alcohol and ether, having a disagreeable pungent odour, melting at 65°, and boiling between 218° and 220° (Seifart, *Zeitschr. f. Chem.* [2] v. 450).

Trichlorophenol, $C^6H^2Cl^3OH$ (iv. 392), produced by the action of dry chlorine on melted phenol, melts at 67°–68°, boils with slight decomposition at 243·5° to 244·5°, volatilises with vapour of water, and exhibits an acid reaction in alcoholic solution. Nitric acid converts it into dichloroquinone:

$$C^6H^3Cl^3O + NO^3H = HCl + NO^2H + C^6H^2Cl^2O^2.$$

The salts produced by boiling trichlorophenol with the carbonates of the alkalis and alkaline earths have an alkaline reaction, and mostly give off trichlorophenol when gently heated. The *potassium salt*, $2C^6H^2Cl^3OK + H^2O$, is easily soluble in water, and crystallises in cauliflower-like masses, appearing under the microscope as furcate groups of capillary needles. The *ammonium salt*, $C^6H^2Cl^3O(NH^4)$, crystallises in large somewhat sparingly soluble needles. The rather sparingly soluble *barium salt*, $(C^6H^2Cl^3O)^2Ba + 4H^2O$, crystallises in radiate groups of laminæ, which give off their water at 140°. The easily soluble *magnesium salt*, $(C^6H^2Cl^3O)^2Mg + 2H^2O$, crystallises with difficulty in circularly grouped pointed needles. On mixing the alcoholic solution of trichlorophenol with neutral lead acetate, a *basic lead salt*, $2(C^6H^2Cl^3O)^2Pb.PbO$, separates in the crystalline form, while the normal salt, $(C^6H^2Cl^3O)^2Pb$, which crystallises in slender prisms, remains in solution. The *silver salt*, $C^6H^2Cl^3OAg$, is a yellow amorphous precipitate. The *ethylic ether*, $C^6H^2Cl^3OC^2H^5$, formed by boiling the potassium salt with ethyl iodide, crystallises in white prisms, melts at 43°–44°, boils at 240°, and is converted by a mixture of sulphuric and nitric acids into a body which crystallises in tufts of needles melting at 53°–54° (A. Faust, *Zeitschr. f. Chem.* [2] iii. 727).

Iodophenols. Schützenberger a. Sengenwald obtained these compounds by the action of iodine chloride on phenol (iv. 394, 409). Körner (*Ann. Ch. Pharm.* cxxxvii. 197) has prepared mono- and tri-iodophenol by treating phenol with iodine and iodic acid, in presence of free alkali and a dilute solution. *Mono-iodophenol*, $C^6H^4I.OH$, is produced, according to the equation:

$$5C^6H^5OH + 2I^2 + IO^3H = 3H^2O + 5C^6H^4IOH.$$

The iodine and iodic acid are first dissolved in the required proportions in dilute potash, the phenol is then added, and the liquid, while constantly stirred, is supersaturated with dilute hydrochloric acid. The precipitated oil, which contains mono-iodophenol, with a small quantity of the tri-iodated compound, is washed with water containing alcohol, and again precipitated from alkaline solution by hydrochloric acid. It is colourless, solidifies at low temperatures, has a strong disagreeable odour, and unites with alkalis, forming salts which are insoluble in concentrated alkali, and are decomposed by carbonic acid. Tri-iodophenol, $C^6H^2I^3OH$, prepared like the preceding compound with the required proportions of the materials, separates on acidulation with hydrochloric acid, as a greyish-white flocculent mass, and crystallises from alcohol of 50 p. c. in interlaced needles, or in large flattened needles like those of benzoic acid. It has a faint but unpleasant odour, melts at 150°, and decomposes when sublimed.

Mono-iodophenol (prepared as above), added to melting caustic potash mixed with so much water that it melts at 165°, is converted into a mixture of the isomeric compounds pyrocatechin and hydroquinone, $C^6H^6O^2$, the latter in the larger proportion, the change consisting in the replacement of I by HO. On precipitating with hydrochloric acid, agitating with ether, and evaporating, there remains a mixture of pyrocatechin and hydroquinone, which may be separated by precipitation with lead acetate (not in excess), the hydroquinone then remaining in solution.

Mono-iodophenol is likewise obtained, by a series of transformations, from nitraniline, namely, by converting this compound into diazonitrobenzene sulphate (iv. 448); this latter into iodonitrobenzene by the action of hydriodic acid: $C^6H^3(NO^2)N^2 + HI = C^6H^4(NO^2)I + N^2$; this into diazo-iodobenzene by the action of nitrous acid; and the diazo-iodobenzene into iodophenol by boiling its nitrate or sulphate with water: $C^6H^3IN^2 + H^2O = C^6H^5IO + N^2$. The iodophenol thus obtained from nitraniline is converted by melting potash wholly into hydroquinone; and that prepared in like manner from β nitraniline or paranitraniline (from dinitrobenzene) yields the isomeric compound resorcin. There are therefore three modifications of mono-iodophenol, yielding by substitution of HO for I, the corresponding modifications of oxyphenol: viz. ortho-iodophenol (1 : 2), yielding hydroquinone; meta-iodophenol (1 : 3), yielding pyrocatechin; and para-iodophenol (1 : 4), yielding resorcin.

The iodophenol obtained by the action of iodine and iodic acid on phenol is a mixture of ortho- and meta-iodophenols, the former predominating (Körner). See AROMATIC SERIES (p. 198).

Hlasiwetz a. Weselsky (*Wien. Akad. Ber.* lx. [2] 290; *Chem. Centr.* 1870, 63) prepare mono- and di-iodophenol by the action of iodine on phenol in alcoholic solution, in presence of an easily reducible metallic oxide which yields an insoluble iodide (mercuric oxide). For mono-iodophenol the proportions are those indicated by the equation:

$$2C^6H^6O + HgO + I^4 = 2C^6H^5IO + HgI^2 + H^2O;$$

but even when these proportions are exactly observed, di-iodophenol is always formed at the same time. The mono-iodophenol is found chiefly in the alcoholic filtrate: the di-iodophenol remains mixed with the mercuric iodide, and may be dissolved out by dilute solution of potassium carbonate, and precipitated by hydrochloric acid. The mono-iodophenol obtained by evaporating the alcoholic liquid yields by decomposition with potassium hydrate, chiefly resorcin (with a little pyrocatechin), and therefore consists mainly of para-iodophenol.

For the preparation of di-iodophenol the best proportions are indicated by the equation:

$$C^6H^6O + HgO + I^4 = C^6H^4I^2O + HgI^2 + H^2O.$$

Crystallised from weak spirit, it forms colourless or slightly greyish, soft, felted crystals, having a silky lustre, and a faint but persistent odour, like that of mono-iodophenol; it dissolves easily in alcohol, ether, and carbon bisulphide; sublimes; melts at 150°; and decomposes at a higher temperature. It is not decomposed by boiling with aqueous or alcoholic potash solution, but when fused with potassium hydrate it yields a considerable quantity of a brown viscid uncrystallisable substance containing a small quantity of pyrocatechin.

Nitrophenols. The crystalline and less volatile modification of mononitrophenol called *isonitrophenol*, which Fritzsche obtained by the action of nitric acid on aqueous phenol (iv. 395), is converted by reduction into an amidophenol, which, when oxidised with potassium chromate and sulphuric acid, yields large quantities of hydroquinone; it is therefore orthonitrophenol (1 : 2). The dinitrophenol prepared from this compound is identical both with that obtained from the more volatile mononitrophenol (iv. 394), and with that which Griess obtained by heating diazodinitrophenol in alcoholic solution. In like manner the two modifications of mononitrophenol yield only one and the same trinitrophenol, or picric acid, melting at 122·5° (Körner). There is at present no evidence to show whether the more volatile mononitrophenol belongs to the meta- or the para- series; it is therefore more convenient still to distinguish the two known modifications as nitro- and iso-nitrophenol (Körner, *Zeitschr. f. Chem.* [2] ii. 662, 731; *Bull. Acad. Belg.* [2] xxiv. 166).

Mononitromethyl-phenol or *Mononitranisol*, $C^6H^4(CH^3)(NO^2)O$, formed by the action of methyl iodide in excess on the silver salt of nitrophenol, is a yellowish fragrant oil boiling at 265°; it solidifies at 0°, melts again at 9°, has a sp. gr. of 1·249 at 26°, and volatilises easily with vapour of water. *Isonitromethyl-phenol* or *Isonitranisol*, prepared like the preceding from silver isonitrophenate, crystallises in large rhombic prisms, melting at 48°, boiling at 258°–260°, and likewise volatilising with vapour of water. Both these compounds are also produced by direct nitration of anisol (Brunck, *Zeitschr. f. Chem.* [2] iii. 202).

Monoamidomethylphenol or *Anisidine*, $C^6H^4(NH^2)(CH^3)O$, produced by reduction of nitranisol with tin and hydrochloric acid, is a colourless oil, which remains liquid below 0°, boils at 216°, and has a sp. gr. of 1·108 at 26°. The hydrochloride, $C^6H^4(NH^2)(CH^3)O.HCl$, crystallises in easily soluble rhombic tables. *Isoamidomethylphenol* or *Isanisidine*, $C^6H^4(NH^2)(CH^3)O$, crystallises from alcohol or ether in colourless prisms, melting at 52°, and volatilising without decomposition. The *hydrochloride* forms easily soluble prisms (Brunck, *loc. cit.*).

Dinitrophenol. $C^6H^4(NO^2)^2O$.—This compound is best prepared by gradually adding a very strong aqueous solution of phenol to commercial nitric acid (sp. gr. 1·4), with constant agitation, till the action becomes feeble. Dinitrophenol then separates in considerable quantity, and after washing with water and crystallisation from alcohol and water, forms thin faintly yellow tables and laminæ, or (from water) nearly colourless, fibro-laminar masses. It volatilises at 70°, passes over also with vapour of water; dissolves in 21 pts. water at 100°, in 197 pts. at 18°, and in 7261 pts. at 0°. Its *silver salt*, $2C^6H^3(NO^2)^2OAg + H^2O$, forms yellow needles, blackened by light, insoluble in ether, slightly soluble in water and alcohol, detonating violently when heated. The *mercuric salt*, obtained by precipitation, forms slightly soluble yellow needles. The *ferric salt*, obtained in like manner, crystallises in green laminæ moderately soluble in water. The *nickel salt*, $[C^6H^3(NO^2)^2O]^2Ni + 8H^2O$, forms green needles. The *manganous salt*, $[C^6H^3(NO^2)^2O]^2Mn + 5H^2O$, crystallises in tufts of rose-coloured easily soluble needles. The *quinine salt*, $C^6H^4(NO^2)^2O . C^{20}H^{24}N^2O^2 + 3H^2O$, is insoluble in ether, nearly insoluble in water, slightly soluble in alcohol, and crystallises from the latter in tufts of long orange-coloured needles, or from water in light yellow laminar masses. The *ethylic ether* (dinitrophenetol), $C^6H^3(NO^2)^2O . C^2H^5$, formed by heating the silver salt with ethyl iodide, crystallises from alcohol in nearly colourless needles blackened by light (compare iv. 399). The *methylic ether* (dinitranisol), $C^6H^3(NO^2)^2O.CH^3$, forms long very slender needles; the *amylic ether* is a heavy colourless oil. *Urea dinitrophenate* forms indistinctly crystalline masses. *Naphthalene dinitrophenate*, $C^6H^4(NO^2)^2O . C^{10}H^8$, crystallises from a solution of the two bodies in alcohol or benzol, in yellow needles. It is soluble in ether and in hot water, and crystallises from the latter in microscopic colourless needles. By prolonged boiling with water, it is decomposed, with continued evolution of naphthalene (Gruner, *J. pr. Chem.* cii. 222).

Trinitrophenol or ***Picric Acid.*** $C^6H^3(NO^2)^3O$.—Pure picric acid melts, according to Körner, at 122·5°; the commercial acid between 114° and 115°.

Casthelaz (*Chem. News*, xv. 140) describes a process for the testing of commercial picric acid, founded on the fact that the pure acid is soluble in ether and in benzol, whereas the impurities (oxalic acid and various salts) are insoluble in those liquids.

Picric acid digested with a concentrated aqueous solution of *iodine chloride* is converted into chloropicrin and chloranil (Stenhouse, *Chem. Soc. J.* [2] ii. 366). Under other circumstances it is converted by the same reagent into chlorodinitrophenol (p. 913).

The following *metallic picrates* have been examined by D. Müller (*Pogg. Ann.* cxxiv. 103) $[NO^2 = X]$:

Manganous salt,	$(C^6H^2X^3O)^2Mn + 5H^2O$,	light yellow rhombic crystals.
Cupric salt,	$(C^6H^2X^3O)^2Cu + 16H^2O$,	green quadratic crystals.
Cadmium salt,	$(C^6H^2X^3O)^2Cd + 7H^2O$,	light yellow rhombic crystals.
Ferrous salt,	$(C^6H^2X^3O)^2Fe + 5H^2O$,	light brown crystals permanent below 100°.
Sodio-magnesic salt,	$\left\{\begin{matrix}(C^6H^2X^3O)^2Mg\\3C^6H^2X^3ONa\end{matrix}\right\} + 9H^2O$,	yellow cauliflower-like crystalline groups.
Sodio-ferrous salt,	$\left\{\begin{matrix}(C^6H^2X^3O)^2Fe\\6C^6H^2X^3ONa\end{matrix}\right\} + 12H^2O$,	„ „ „
Sodio-cobaltous salt,	$\left\{\begin{matrix}(C^6H^2X^3O)^2Co\\6C^6H^2X^3ONa\end{matrix}\right\} + 12H^2O$,	„ „ „
Sodio-nickel salt,	$\left\{\begin{matrix}(C^6H^2X^3O)^2Ni\\6C^6H^2X^3ONa\end{matrix}\right\} + 12H^2O$,	„ „ „
Sodio-zinc salt,	$\left\{\begin{matrix}(C^6H^2X^3O)^2Zn\\6C^6H^2X^3ONa\end{matrix}\right\} + 12H^2O$,	„ „ „
Sodio-cadmic salt,	$\left\{\begin{matrix}(C^6H^2X^3O)^2Cd\\6C^6H^2X^3ONa\end{matrix}\right\} + 12H^2O$.	„ „ „
Aluminium salt,	$4C^6H^2X^3O . Al^2O^3 + 16H^2O$,	yellow needles.
Ferric salt,	$4C^{12}H^2X^3O . Al^2O^3 + 16H^2O$,	reddish-yellow needles.

1 pt. of *potassium picrate* requires for solution: of water, 273·3 pts. at 0°, and 440·8 pts. at 20°; of alcohol, 1138 pts. at 0°, and 735·5 pts. at 20° (Frisch, *J. pr. Chem.* c. 229).

Picrate of Triethylrosaniline is one of the varieties of aniline green (Alfraisse, *Dingl. pol. J.* clxxxvi. 324; *Jahresb.* 1867, p. 964).

Ethyl Picrate, $C^6H^2(NO^2)^3O . C^2H^5$, is easily obtained by digesting dry silver picrate (prepared by mixing a hot solution of picric acid with silver carbonate, boiling for a few minutes and filtering) with five times its weight of ethyl iodide at 100°, distilling off the excess of the latter, and repeatedly treating the residue with hot alcohol. The ether, when washed and repeatedly crystallised from alcohol, forms slightly yellowish needles an inch or two long, becoming darker on exposure to light. It is somewhat soluble in hot water, also in ethyl iodide, common ether, carbon bisulphide, and benzol; melts at 78·5°, solidifies at 73°, and decomposes with slight detonation at a higher temperature (H. Müller a. Stenhouse, *Chem. Soc. J.* [2] iv. 235).

Picrates of Hydrocarbons.—Picric acid, as already shown by Fritzsche (iv. 405), affords characteristic reactions for the detection of certain hydrocarbons. For this purpose it is convenient to use an alcoholic solution of the acid saturated at 20°–30°, and either: (1) add the hydrocarbon to the cold-saturated alcoholic solution; or

(2) mix the picric acid solution with a hot alcoholic solution of the hydrocarbon; or (3) dissolve the hydrocarbon, with aid of heat, in the picric acid solution. The following combine under these circumstances with picric acid: ***Naphthalene*** is the only solid hydrocarbon whose cold-saturated alcoholic solution is precipitated by picric acid. The compound forms delicate stellate groups of yellow needles, easily soluble in alcohol. *Retene* treated by method 2 or 3 forms similar needles of an orange-yellow colour. ***Anthracene*** also forms ruby-coloured needles still more soluble than the preceding; the red alcoholic solution is decolorised by addition of a little more alcohol. Other hydrocarbons contained in crude anthracene exhibit the same reaction, which appears to be peculiar to anthracene and its homologues. The hydrocarbon boiling at 260° which exists in crude anthracene, likewise forms, when dissolved in the alcoholic solution of picric acid at the boiling heat, a compound crystallising in orange-yellow needles. ***Chrysene*** forms a granular yellow precipitate, obtainable only by method 3, and consisting of microscopic needles united in scales. In presence of benzerythrene the scales pass into brown spherical groups of needles. ***Benzerythrene*** boiled with an alcoholic solution of picric acid deposits brown-yellow flocks on cooling. The forms of these compounds, when examined by the microscope, are characteristic of the individual hydrocarbons, and easily distinguished from those of picric acid itself, which sometimes separates out; they may also be obtained with mixtures, inasmuch as these mixtures, excepting that of chrysene and benzerythrene, still yield the picrates of the several compounds contained in them. In mixtures of hydrocarbons all of which combine with picric acid, the separation may in many cases be effected by fractional precipitation (Berthelot, *Bull. Soc. Chim.* [2] vii. 30).

BROMONITROPHENOL, $C^6H^4Br(NO^2)O$, obtained by the action of bromine on the more volatile nitrophenol, crystallises from alcohol in shining, yellow, sublimable laminæ, easily soluble in alcohol and ether, melting at 88°. Its *potassium salt*, $C^6H^3Br(NO^2)OK + 2H^2O$, forms long pointed four-sided needles, of a blood-red colour, moderately soluble in water, drying up over sulphuric acid to a dark red powder. The *barium salt*, $[C^6H^3Br(NO^2)O]^2Ba$, crystallises in anhydrous scales of dark red colour and golden lustre. The *silver salt*, $C^6H^3Br(NO^2)OAg$, forms a dark red precipitate or blood-red laminæ having a golden lustre. *Bromisonitrophenol*, $C^6H^4Br(NO^2)O$, produced by the action of 1 mol. bromine on isonitrophenol, is not volatile without decomposition, and crystallises from aqueous alcohol or from ether in long satiny needles melting at 102°. The easily soluble potassium salt forms red crystalline crusts; the sodium salt lemon-yellow needles; the silver salt slender red needles (Brunck).

Dibromonitrophenol, $C^6H^3Br^2(NO^2)O$, is obtained (together with bromopicrin) by adding dibromophenol to a cooled mixture of nitric and sulphuric acid; when separated from its potassium salt and recrystallised from alcohol, it forms large easily sublimable prisms melting at 119°. Its *potassium salt*, $C^6H^2Br^2(NO^2)OK$, forms scarlet needles slightly soluble in cold water, more soluble in boiling water and in alcohol; the *barium salt* is an orange-red, the *silver salt* a brown-red precipitate. The *methylic ether*, precipitated by water from a solution of methylic dibromophenate in fuming nitric acid, crystallises from alcohol in colourless needles (Körner, *Ann. Ch. Pharm.* cxxxvii. 197; *Zeitschr. f. Chem.* [2] ii. 148). *Dibromisonitrophenol*, $C^6H^3Br^2(NO^2)O$, produced by the action of 2 mol. bromine on isonitrophenol, forms beautiful prismatic crystals sparingly soluble in water, easily in alcohol and ether, melting at 141°, and decomposing at a slightly higher temperature without subliming; the *potassium salt* in tufts of orange-yellow anhydrous needles, or in light yellow laminæ containing 2 mol. water; the *barium salt*, $[C^6H^2Br^2(NO^2)O]^2Ba + 10H^2O$, in light yellow needles which crumble to a red powder; the *silver salt*, $C^6H^2Br^2(NO^2)OAg$, forms sparingly soluble yellowish needles (Brunck, *loc. cit.*).

CHLORONITROPHENOLS.—*Mononitrochlorophenol*, $C^6H^4Cl(NO^2)O$, is prepared by passing 200 grms. of chlorine gas into 500 grms. pure phenol not cooled, and gradually adding the resulting chlorophenol to 1000 grms. nitric acid of sp. gr. 1·4, previously diluted with 1500 grms. water. The mixture is left for four days, being frequently stirred, but not heated; the chloronitrophenol which collects at the bottom in lumps is collected, washed, and converted into sodium salt; this salt, after recrystallisation, is decomposed with hydrochloric acid; and the chloronitrophenol thereby separated is distilled with vapour of water and purified by recrystallisation from hot alcohol, ether, and chloroform. It crystallises from hot alcohol in needles, from chloroform in large light yellow triclinic prisms having the form of cupric sulphate; has a strong saffron-like odour, and melts at 86°–87°. It dissolves easily in chloroform and ether, less easily in alcohol, and is nearly insoluble in water. Its salts crystallise easily and well, dissolve sparingly in cold, more easily in hot water. The *ammonium salt*, $C^6H^3Cl(NO^2)ONH^4$, forms long orange-red needles, volatilising with vapour of water; the *sodium salt*, $C^6H^3Cl(NO^2)ONa + H^2O$, crystallises in red prisms; the *barium salt*, $[C^6H^3Cl(NO^2)O]^2Ba + 2H^2O$, in short red prisms; the *silver salt*, $C^6H^3Cl(NO^2)OAg$, in brownish-red needles, very slightly soluble in water. The *ethylic ether*, $C^6H^3Cl(NO^2)OC^2H^5$, obtained by heating the silver salt with ethyl iodide, crystallises in yellowish-white needles or laminæ, having an unpleasant odour, and melting at 61°–62° (Faust a. Saame, *Zeitschr. f. Chem.* [2] v. 450).

Chloramidophenol Hydrochloride, $C^6H^4Cl(NH^2)O.HCl$, separates from the cooled solution obtained by reducing chloronitrophenol with tin and hydrochloric acid, and may be purified by recrystallisation from hot water. It crystallises in white laminæ easily soluble in water and permanent in the air. The corresponding *sulphate* forms stellate groups of needles (Faust a. Saame).

Dichloronitrophenol, $C^6H^3Cl^2(NO^2)O$, obtained by adding crystalline dichlorophenol (p. 908) to fuming nitric acid, precipitating with water, and recrystallising from alcohol, appears to be identical with the nitro-compound which Laurent obtained in like manner from liquid dichlorophenol (iv. 397). It forms yellow crystalline laminæ, melting at 121°–122°, sparingly soluble, but with deep yellow colour, in water, sublimes slowly at 100°, and detonates when suddenly heated. Its *ammonium salt*, $C^6H^2Cl^2(NO^2)ONH^4$, crystallises in shining, deep orange-coloured, sublimable needles; a small quantity of its dust excites violent sneezing. The *sodium salt* forms nodular groups of orange-red needles; the *potassium salt*, long shining needles having nearly the colour of chromic acid. The *silver salt* crystallises from a large quantity of boiling water in tufts of very dark red needles. The *magnesium* and *barium salts* form silky orange-yellow needles, slightly soluble in water. The *basic lead salt*, $C^6H^2Cl^2(NO^2)O.Pb.OH$, is an orange-coloured precipitate. The *ethylic ether*, $C^6H^2Cl^2(NO^2)O.C^2H^5$, obtained by adding ethylic dichlorophenate to fuming nitric acid, crystallises from absolute alcohol in large, flattened, nearly colourless prisms, melting at 29°. Dichloronitrophenol digested with tin and hydrochloric acid yields a double stannous salt (colourless when freshly prepared), which after separation of the tin by hydrogen sulphide, yields *dichloramidophenol hydrochloride*, $C^6H^3Cl^2(NH^2)O.HCl$, in colourless laminæ, quickly reddening on exposure to light, easily soluble in water and alcohol. *Dichloramidophenol*, $C^6H^3Cl^2(NH^2)O$, separated therefrom, forms small white silky crystals which decompose very easily, especially when moist (Fischer, *Zeitschr. f. Chem.* [2] iv. 386).

Faust a. Saame have obtained dichloronitrophenol, with properties exactly the same as those above described, by passing 1 at. chlorine into monochloronitrophenol. Its *barium salt* forms orange-yellow needles containing $[C^6H^2Cl^2(NO^2)O]^2Ba + 2H^2O$.

Dichloro-isonitrophenol or *Dichlor-orthonitrophenol*, $C^6H^3Cl^2(NO^2)O$, is obtained by saturating fused orthonitrophenol with chlorine, and may be purified by converting it into a barium salt, recrystallising this salt several times, with addition of animal charcoal, and decomposing it with hydrochloric acid. When separated from a warm solution, it forms a heavy, nearly colourless, easily crystallising oil; dissolves easily in alcohol, ether, and chloroform, crystallises from ether in long slightly yellowish rhombic prisms or tables, from chloroform in flat shining colourless needles. Heated with water it melts, but is not perceptibly dissolved. It has a faint phenolic odour, does not volatilise with vapour of water, and is but slightly sublimable. Melts with decomposition at 125°. Its *ammonium salt*, $C^6H^2Cl^2(NO^2)ONH^4 + H^2O$, forms long shining yellow needles, which give off their water and become colourless when left over sulphuric acid; dissolves easily in hot, sparingly in cold water. The *sodium salt*, $C^6H^2Cl^2(NO^2)ONa + 5H^2O$, forms yellow shining needles, easily soluble in water and alcohol. The *barium salt*, $[C^6H^2Cl^2(NO^2)O]^2Ba + 4H^2O$, crystallises, according to concentration, in brown-red metallically lustrous prisms or laminæ, or in light-red flat needles; dissolves easily in boiling water, sparingly in cold water. The *calcium salt*, $[C^6H^2Cl^2(NO^2)]^2Ca + 9H^2O$, crystallises in golden-yellow shining needles or laminæ very soluble in water; the *magnesium salt*, $[C^6H^2Cl^2(NO^2)O]^2Mg + 10H^2O$, in rosettes of yellow needles, very soluble in water. The *silver salt*, $C^6H^2Cl^2(NO^2)OAg$, forms colourless interlaced needles, quickly turning yellow, and very sparingly soluble in water. The *lead salt*, $[C^6H^2Cl^2(NO^2)O]^2Pb + 4\frac{1}{2}H^2O$, forms very sparingly soluble, serrated, dull yellow needles, which easily give off their water. The *copper salt* forms dingy green needles, decomposing even below 100°. The *ethylic ether*, obtained from the silver salt by means of ethyl iodide, is a colourless body very much like phenol, melting at 135° (Seifart, *Zeitschr. f. Chem.* [2] v. 449).

Dichlor-orthoamidophenol, $C^6H^3Cl^2(NH^2)O$, obtained by reducing the dichloronitro-compound with tin and hydrochloric acid, crystallises from water in sparingly soluble colourless striated laminæ, which easily turn brown. It dissolves easily in alcohol, sublimes in colourless laminæ when very slowly heated, melts at 165°–166°. The *sulphate*, $[C^6H^2Cl^2(NH^2)O]^2.SO^4H^2 + 3H^2O$, crystallises from a boiling saturated aqueous solution in needles slightly soluble in hot alcohol. The *hydrochloride*, $C^6H^2Cl^2(NH^2)O.HCl$, also crystallises in needles, decomposing easily in solution, melting below 230°, subliming completely in white laminæ (Seifart).

Chlorodinitrophenol. $C^6H^3Cl(NO^2)^2O$.—This compound is known in two modifications, which may be distinguished as *a* and *β*. *a Chlorodinitrophenol* is obtained by the action of nitric acid on monochlorophenol (Dubois, *Zeitschr. f. Chem.* [2] iii. 205), or by adding monochloronitrophenol to red nitric acid (Faust a. Saame, *ibid.* v. 451). It crystallises from alcohol in yellow needles, from chloroform in large monoclinic prisms resembling sugar-candy, and has a great tendency to form twin-crystals. It melts at 81°, resolidifies at 69°, volatilises without decomposition when slowly heated, dissolves sparingly in cold, more easily in boiling water.

β Chloronitrophenol was obtained by Faust a. Saame from the residue left after the mononitrochlorophenol, prepared as above described, had been distilled off with aqueous vapour. This residue was added to red nitric acid, the dark solution precipitated by water, the precipitate converted into an ammonium salt; and this salt after repeated crystallisation was decomposed by hydrochloric acid. *β* chlorodinitrophenol thus obtained crystallises from hot water and dilute alcohol in yellowish laminæ, from chloroform in irregular six-sided prisms melting at 111°. It is more soluble in hot water than the *a* modification. The *ammonium salt*, $C^6H^2Cl(NO^2)^2ONH^4 + H^2O$, crystallises in yellow needles; the *barium salt*, $[C^6H^2Cl(NO^2)^2O]^2Ba + 9H^2O$, in short yellow needles, brick-red when dehydrated. The *silver salt*, $C^6H^2Cl(NO^2)^2OAg + H^2O$, separates from hot water in a bulky mass of slender yellow needles. These salts are likewise more soluble in hot than in cold water.

γ Chlorodinitrophenol, the modification which Griess obtained by passing a strong stream of chlorine into phenol, and adding the product by small portions to nitric acid of ordinary strength (iv. 400), is more easily prepared, according to Stenhouse (*Chem. Soc. J.* [2] v. 435), by the action of iodine chloride on picric acid. Chlorine gas is passed into a mixture of 8 pts. picric acid, 3 pts. water, and 1 pt. iodine, kept in gentle ebullition in a flask provided with an upright condensing tube, till carbon dioxide and nitrogen dioxide are given off and no more oily drops of chloropicrin are produced. The iodine chloride having been distilled off at 120°, the crystalline residue is washed with cold water and recrystallised from hot water. The chlorodinitrophenol thus obtained crystallises in yellow laminæ melting at 103°, volatilising slightly at 100°, more easily with aqueous vapour.

On the constitution of the chloronitrophenols, see Petersen (*Ann. Ch. Pharm.* [1871] cxlvii. 171; *Chem. Soc. J.* [2] ix. 248).

IODONITROPHENOLS (Körner, *Bull. Acad. Belg.* [2] xxiv. 166; *Jahresb.* 1867, p. 616).—These compounds are formed by treating the nitrophenols in alkaline solution with a mixture of iodine and iodic acid, in proportions indicated by equation I. for the mono-iodated, and by equation II. for the di-iodated compounds:

$$\text{I.}\quad 5C^6H^{5-x}(NO^2)^xOH + 2I^2 + IO^3H = 5C^6H^{4-x}I(NO^2)^xOH + 3H^2O$$
$$\text{II.}\quad 5C^6H^{5-x}(NO^2)^xOH + 4I^2 + 2IO^3H = 5C^6H^{3-x}I^2(NO^2)^xOH + 6H^2O$$

They are precipitated from these solutions by hydrochloric acid in the form of powder, or in fused yellowish masses; if iodine still separates, the mixture must be once more supersaturated with alkali.

Iodisonitrophenol or *Iodorthonitrophenol*, $C^6H^4I(NO^2)O$, crystallises from a hot-saturated aqueous solution in yellow needles, melting at 93°, at a lower temperature under water, not volatile without decomposition. It is also formed by the action of hydriodic acid on diazonitrophenol, but when thus prepared it can be obtained pure (melting at 94°) only by repeated crystallisation from boiling carbon bisulphide. Its easily soluble *potassium salt* crystallises from water in yellow needles, from alcohol with 3 mol. water, in lemon-yellow prisms. The *sodium salt*, $2C^6H^3I(NO^2)ONa + 5H^2O$, forms golden-yellow elliptic scales; the *barium salt*, reddish-yellow needles; the *silver salt* is a lemon-yellow precipitate somewhat soluble in hot water, and crystallising therefrom in needles. *Iodonitrophenol* from volatile nitrophenol is golden-yellow, and crystallises readily, but has not been further examined.

Di-iodisonitrophenol, $C^6H^3I^2(NO^2)O$, crystallises from ethereal solution in colourless prisms, which turn yellow on exposure to the air, melt at 156·5°, and decompose at a higher temperature. The *potassium salt*, $C^6H^2I^2(NO^2)OK$, forms golden-yellow needles with violet iridescence; the *sodium salt*, orange-yellow efflorescent laminæ; the *silver salt* is a yellowish, nearly insoluble precipitate. *Di-iodo-*

nitrophenol (from volatile nitrophenol) crystallises from a mixture of alcohol and ether in slender dark-yellow needles; from ether in large prisms having a glassy lustre. It is slightly soluble in water, melts at 98°. The easily soluble *potassium salt*, $C^6H^2I^2(NO^2)OK$, crystallises in red-brown needles; the *sodium salt*, $C^6H^2I^2(NO^2)ONa + H^2O$, from alcoholic solution in dark brown prisms having a golden lustre, and yielding a blood-red powder; the silver salt is a black-brown precipitate.

Iodobromisonitrophenol, $C^2H^3IBr(NO^2)O$, prepared from bromoisonitrophenol by the general process above given, is insoluble in water, slightly soluble in alcohol, easily soluble in ether, and crystallises from this solution in colourless prisms. The potassium salt, $C^6H^2IBr(NO^2)OK$, forms tufts of yellow needles. *Iodobromonitrophenol* (from volatile nitrophenol) crystallises from ether in orange-coloured prisms, melts at 104·2°, and volatilises with vapour of water. Its salts are sparingly soluble; the *potassium salt* crystallises in anhydrous flat prisms having a brown colour and bright metallic lustre; the *sodium salt* with 1 mol. water in dark brown prisms; the *barium*, *lead*, and *silver salts* are dark brown precipitates.

Iodo-dinitrophenol, $C^6H^3I(NO^2)^2O$, is nearly insoluble in water, soluble in alcohol and ether, and crystallises from alcoholic solution in vitreous sulphur-yellow prisms. It melts under boiling water and volatilises with aqueous vapour. The *potassium salt*, $C^6H^2I(NO^2)^2OK + 2H^2O$, crystallises from aqueous solution in yellow laminæ or needles; the *barium salt* in yellow, slightly soluble laminæ. A similarly composed and probably identical compound is produced by the action of hydriodic acid on diazodinitrophenol; but its potassium salt crystallises in orange-red anhydrous needles.

From the results just described, and from those obtained by Brunck with the bromonitrophenols (p. 912), Körner concludes: (1) That the places occupied by the nitroxyl in dinitrophenol are those which it occupies in isonitrophenol and in volatile nitrophenol; (2) that in the partial reduction of dinitrophenol, that atom of nitroxyl which corresponds to volatile nitrophenol gives place to amidogen; and (3) that in volatile nitrophenol the nitroxyl occupies one of two places, symmetrically situated with regard to the hydroxyl [that is to say, that it belongs to the meta- series].

Reduction-derivatives of the Nitrophenols: Amidophenols.

The amidophenols obtained by reduction of mononitrophenol and its chlorinated derivatives have been already noticed (pp. 910, 913).

From trinitrophenol or picric acid three amidophenols may be derived, viz.,

$C^6H^2(NO^2)^2(NH^2)OH$	$C^6H^2(NO^2)(NH^2)^2OH$	$C^6H^2(NH^2)^3OH$
Amidodinitrophenol.	Diamidonitrophenol.	Triamidophenol.

The first, generally known as *picramic acid*, was obtained by Girard in 1853, by reducing picric acid with hydrogen sulphide. According to C. D. Braun (*Zeitschr. f. Chem.* [2] i. 744), it is produced from picric acid by the action of potassium ferrocyanide, and more quickly in presence of alkali, by grape-sugar. Petersen (*Zeitschr. f. Chem.* [2] iv. 377) has examined some of its compounds with acids. The *hydrochloride*, $C^6H^3(NO^2)^2(NH^2)O.HCl$, separates from a hot-saturated solution in concentric groups of red-brown needles, soluble in alcohol and ether, giving off their hydrochloric acid partially on exposure to the air, completely at 80°. The *platinochloride*, $2(C^6H^3(NO^2)^2(NH^2)O.HCl).PtCl^4$, separates from concentrated solution in small yellow granular crystals. The *nitrate*, obtained by decomposing the hydrochloride in alcoholic solution with silver nitrate, crystallises in brown-red laminæ. When a solution of amidodinitrophenol in cold strong sulphuric acid is diluted with water, the amidodinitrophenol is precipitated, and the solution yields brown crystals containing sulphuric acid.

Girard and Pugh found that picramic acid is converted by nitric acid into picric acid; but according to Wöhler and Carey Lea, this is not the case (iv. 406). Stenhouse (*Chem. Soc. J.* [2] vi. 150), by treating 1 pt. picramic acid with 3 pts. boiling nitric acid of sp. gr. 1·45, has obtained crystals of diazodinitrophenol, $C^6H^2N^2(NO^2)^2O$, together with a comparatively small quantity of picric acid, which remains in the mother-liquor.

Lautemann (iv. 640), by treating picric acid with iodine and phosphorus, obtained the hydriodide of picramine, $C^6H^3(NH^2)^3$, a base derived from picric acid by substitution of $(NH^2)^3$ for $(NO^2)^3$, and simultaneous reduction of the hydroxyl-group HO; and according to Beilstein (*Ann. Ch. Pharm.* cxxx. 242), the same base is obtained by reduction of picric acid with tin and hydrochloric acid. Heintzel (*Zeitschr. f. Chem.* [2] iii. 339) finds that the base obtained by either of these modes of reduction is not picramine, but tri-amidophenol, while, on the other hand, Gauhe (*ibid.* iv. 90) confirms Lautemann's results as to the formation of picramine hydriodide,

$C^6H^3(NH^2)^3.3HI$, by the action of iodine and phosphorus on picric acid, and regards the salt which Heintzel obtained by the same process, not as the hydriodide of triamidophenol, but as the trihydriodide of picramine contaminated with phosphoric acid.

Triamidophenol. $C^6H^2(NH^2)^3OH$.—A mixture of 1 pt. picric acid, 4 pts. tin, and 15 pts. crude hydrochloric acid, when gently warmed, begins to boil in a few minutes, and the filtered liquid deposits on cooling quadratic laminæ, which after drying over lime in a vacuum, have, according to Heintzel, the composition of *triamidophenol stannochloride*, $C^6H^2(NH^2)^3OH.3HCl.SnCl^2$ [according to Beilstein, that of picramine stannochloride, $C^6H^3(NH^2)^3.3HCl.SnCl^2$]. This salt dissolves in water, alcohol, and ether, and after recrystallisation from water contains 1½ mol. water (5·8 p. c.). It is partially decomposed by repeated crystallisation from a slightly acid aqueous solution, but from a solution containing a large excess of hydrochloric acid it separates without decomposition in fan-shaped groups of long needles. The alcoholic or ethereal solution of the salt acquires a deep blue colour; so likewise does the aqueous solution when much diluted; ferric chloride produces the same colour. The *hydrochloride*, $C^6H^2(NH^2)^3OH.3HCl$, obtained by removing the tin from the preceding salt by hydrogen sulphide, is easily soluble in water, less soluble in alcohol and ether, and separates by slow evaporation in a vacuum, in nodular groups of yellow needles; the concentrated solution imparts a permanent green-black colour to the skin, also to wool and silk. The *sulphate*, $2C^6H^2(NH^2)^3OH.3SO^4H^2$, is deposited on mixing the concentrated solution of the hydrochloride with dilute sulphuric acid, in white curdy flocks, which when moist gradually change to dark-coloured rhombohedral crystals. The *hydroferrocyanide*, $2C^6H^2(NH^2)^3OH.Fe^2H^4Cy^6$, is a white crystalline precipitate, slightly soluble in water and in alcohol; potassium ferrocyanide also forms a white precipitate.

Amido-diimidophenol Hydrochloride, $C^6H^2(NH^2)(NH)^2OH.HCl$ * (?), is gradually deposited from a concentrated solution of triamidophenol hydrochloride, in brown crystals having a blue lustre by reflected light, insoluble in ether, slightly soluble in alcohol, easily and with splendid blue colour in water; decomposed by hot water. The blue solution heated with dilute hydrochloric or sulphuric acid becomes red, and deposits white needles, having nearly the composition of the *hydrochloride of amid-imid-hydroxyphenol*, $C^6H^2(NH^2)(NH)(OH)^2.HCl$ * (?) (Heintzel).

PHENOLIC ETHERS. *Ethyl-phenol* or *Phenetol.* $C^8H^{10}O = C^6H^5.(C^2H^5)O$ (Fittig a. Kiesow, *Zeitschr. f. Chem.* [2] v. 333. Beilstein a. Kuhlberg, *ibid.* 461; *Chem. Centr.* 1870, 45).—This compound, originally obtained by the dry distillation of barium ethyl-salicylate (iv. 391), may also be prepared by heating the potassium salt of ethyl-benzene-sulphuric acid with 3 pts. of potassium hydrate to 270°–280° for some hours, acidulating with sulphuric acid, and distilling. The ethyl-phenol, which passes over with the first portions of aqueous vapour, is separated from the water, left some time in contact with calcium chloride, and subjected to fractional distillation, the greater part passing over between 208° and 210°. This portion solidifies on cooling in large transparent prismatic crystals, very much like phenol, which may be freed from an adhering viscid oil by pressure between bibulous paper in the exsiccator. The crystalline compound is ethyl-phenol. It melts at 47°–48° and boils at 209°–210° (Fittig a. Kiesow); melts at 46° and boils at 214°–215° (Beilstein a. Kuhlberg), but volatilises even at ordinary temperatures. In contact with water it instantly liquefies, whence it seems to follow that liquid ethyl-phenol (iv. 391) is rather a hydrate than an isomeric modification (Fittig a. Kiesow). On the other hand, the liquid ethyl-phenol expressed from the crystals as above mentioned does not solidify even in a freezing mixture; it boils at 212° (Beilstein a. Kuhlberg).

Ethyl-phenol treated with sodium and carbon dioxide is converted into ethyl-(para- or meta-) oxybenzoic acid: $C^6H^5(C^2H^5)O + CO^2 = C^7H^5(C^2H^5)O^3$ (Beilstein a. Kuhlberg). See PARAOXYBENZOIC ACID (p. 899).

Methyl-phenol. $C^6H^5(CH^3)O$.—See ANISOL (i. 365).

Chloromethyl-phenol, $C^6H^4Cl(CH^3)O$, is produced by the action of phosphorus pentachloride on anisol. It is a colourless liquid having a rather agreeable odour, a sp. gr. of 1·182 at 9°, and boiling at about 200°. Insoluble in water and in alkalis, soluble in alcohol and in ether; dissolved by strong nitric acid with rise of temperature, but without evolution of gas (L. Henry, *Zeitschr. f. Chem.* [2] vi. 247).

Bromethyl-phenol, $C^6H^4Br(CH^3)O$, obtained in like manner, boils at 220°, and has a sp. gr. of 1·494 at 9° (Henry).

Chlorethyl-phenol, $C^6H^4Cl(C^2H^5)O$, resembles the methyl-compound in external character, boils at 210°, and has a sp. gr. of 1·106 at 9° (Henry).

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* These formulæ are inadmissible, inasmuch as the imidogen, which is essentially a bivalent radicle, enters into them as univalent.

Ethylene-diphenol. $C^{14}H^{14}O^2 = C^{12}H^{10}(C^2H^4)''O^2$ (Lippmann, *Chem. Centr.* 1780, p. 45. Burr, *Zeitschr. f. Chem.* [2] v. 165).—Produced by heating 1 mol. ethylene bromide with 2 mol. finely pulverised potassium-phenol in a sealed tube to 140°. Forms small laminæ, melting at 98·5° (Burr), 95° (Lippmann), and burning with a very smoky flame when heated on platinum foil. Insoluble in water, slightly soluble in cold alcohol, easily in boiling alcohol and cold chloroform (Lippmann); soluble also in ether, from which it separates in shining imperfectly developed crystals (Burr). When heated with strong nitric acid it is converted into an acid compound crystallising in needles of a deep yellow colour, and soluble in ether (Burr).

Ethylene-diphenol tetrabromide, $C^{14}H^{14}O^2Br^4$, is produced by dropping bromine into a solution of ethylene-diphenol in chloroform, heating the product for some hours to 100°, and crystallising from hot chloroform. It forms small interlaced needles melting above 100°.

Ethylene-diphenol-sulphuric acid, $C^{14}H^{14}S^2O^8 = C^{12}H^8(C^2H^4)''(SO^4H)^2$, is formed by adding strong sulphuric acid to ethylene-diphenol heated to 120°, and keeping the mixture for some time at 100°. On saturating the liquid with lead carbonate, filtering, washing with hot water, and evaporating, the *lead salt*, $C^2H^4(C^6H^4SO^4)^2Pb$ (at 120°), crystallises in laminæ soluble in hot water. The *barium salt* is a fine crystalline powder slightly soluble in hot water (Lippmann).

Isopropyl-phenol, $C^6H^5(C^3H^7)O$, is obtained by heating isopropyl iodide with sodium-phenol, either to 110°–120° in sealed tubes, or in a retort with reversed condenser. When purified by precipitation with water, washing with potash-solution, and distillation, it forms a colourless, rather viscid liquid, smelling somewhat like geraniums. It boils at 176°, and has a sp. gr. of 0·958 at 0°, 0·947 at 12·5°. Vapour-density obs. = 5·00; calc. = 4·73. Index of refraction for the yellow sodium line = 1·5124. Inactive to polarised light.

Isopropyl-monobromophenol, $C^6H^4Br(C^3H^7)O$, is the chief product formed by gradually adding 1 mol. bromine to 1 mol. isopropyl-phenol. It is a somewhat viscid liquid, smelling like anisol, insoluble in water, soluble in alcohol, and more easily in ether. Boils at 236°. Sp. gr. = 1·981 at 0°; 1·957 at 12·5°. Index of refraction for the yellow sodium line = 1·553. Inactive to polarised light.

By using an excess of bromine, more highly brominated products are obtained. The resulting crystalline mass dissolves completely in potash, and on adding hydrochloric acid, tribromo-isopropyl-phenol is precipitated, melting at 93° (Silva, *Bull. Soc. Chim.* [2] xiii. 27; *Zeitschr. f. Chem.* [2] vi. 249).

PHENOMALIC ACID. $C^6H^{10}O^5$ (Carius, *Ann. Ch. Pharm.* cxlii. 129; *Jahresb.* 1866, p. 560).—An acid homologous with malic acid, produced by reduction of trichlorophenomalic acid (*infra*), namely, by heating the concentrated aqueous solution of the latter with zinc-powder, assisting the action towards the end by gradual addition of hydrochloric acid till the zinc is completely dissolved. The reaction being completed, the liquid is neutralised with baryta-water, the zinc precipitated by barium sulphide, and the hydrochloric acid removed by repeatedly evaporating the solution, which when decolorised with animal charcoal and evaporated, leaves the phenomalic acid in the form of a colourless amorphous deliquescent mass. The same acid is formed by the action of more powerful reducing agents on trichlorophenomalic acid, but in that case it undergoes a further transformation into succinic acid and a body having the composition of acetic aldehyde, ($C^6H^{10}O^5 = C^4H^6O^4 + C^2H^4O$), which latter, however, is converted into an amorphous acid, or completely decomposed with separation of charcoal, according to the circumstances of the experiment.

Trichlorophenomalic Acid. $C^6H^7Cl^3O^5$ (Carius, *loc. cit.*).—Produced by the action of chlorous acid on benzene:

$$C^6H^6 + 3ClHO^2 = H^2O + C^6H^7Cl^3O^5.$$

The best way of preparing it is to add potassium chlorate (150 grms.) by small portions to a mixture of benzene (80 grms.) and sulphuric acid (1200 grms.) diluted with half its weight of water, agitating after each addition, and cooling the vessel if necessary; then, after 3 or 5 days, heating the mixture to about 70° and adding sufficient warm water to prevent the potassium sulphate from crystallising out. The greater part of the trichlorophenomalic acid is then contained in the watery liquid (the rest in the brownish supernatant oil), and may be extracted by agitating with ether, evaporating the latter, dissolving the residue, consisting of trichlorophenomalic, sulphuric, and oxalic acids, in water, precipitating the sulphuric acid with barium chloride, and again treating with ether. From the viscid residue left on distilling off the ether, the trichlorophenomalic acid partly crystallises out, either in a vacuum or after heating for some hours to 40°–50°, and a further portion separates after addition of water sufficient to produce permanent turbidity. It is purified by recrystallisation from a quantity of hot water large enough to prevent it from separating as an oil on cooling.

Trichlorophenomalic acid crystallises in monoclinic forms, from the hot aqueous solution in laminæ; by slow evaporation, or from other solvents, in tables or prisms with pyramidal faces. It melts at 131°–132°, with partial volatilisation, but without decomposition, and solidifies on cooling to a crystalline mass of sp. gr. about 1·5; when slowly heated above its melting point, it is resolved, almost without residue, into water and white vapours of a new acid; when quickly heated to 180°, it decomposes, with strong intumescence and separation of charcoal. It dissolves sparingly in cold, easily in hot water, alcohol, ether, and warm benzol. The aqueous solution has an acid reaction, decomposes carbonates, gives white precipitates with silver and lead salts on cautious addition of ammonia, and does not prevent the precipitation of ferric salts by ammonia. It decomposes partially on exposure to light, assuming a reddish colour, very quickly on boiling, with formation of hydrochloric acid, and completely by heating with baryta-water, whereby it is converted into phenaconic acid, $C^6H^6O^6$ (p. 904). It does not appear to form a nitro-compound, but is decomposed by boiling with nitric acid, and more quickly by potassium chlorate and sulphuric acid, yielding oxalic acid; heated in solution with a small quantity of silver nitrate and ammonia, it throws down metallic silver. By nascent hydrogen it is reduced to phenaconic acid, and by stronger action to succinic acid; this last transformation is produced by heating the trichlorophenomalic acid to 150°–180° in a sealed tube with saturated aqueous hydriodic acid; also by the action of tin and hydrochloric acid (Carius).

PHENYL or **DIPHENYL.** $C^{12}H^{10}$.—This hydrocarbon is formed, together with others, when benzene-vapour is passed through a red-hot tube: $2C^6H^6 = C^{12}H^{10} + H^2$; also, together with benzene, by passing chrysene-vapour mixed with hydrogen through a red-hot tube: $C^{18}H^{12} + 2H^2 = C^{12}H^{10} + C^6H^6$ (Berthelot, p. 459). Heated for an hour in a sealed tube filled with *hydrogen* it is partly resolved into benzene and chrysene, the latter being probably formed by polymerisation of phenylene produced in the first instance:

$$\begin{array}{ccccccccc} C^{12}H^{10} & = & C^6H^6 & + & C^6H^4; & \text{and} & 3C^6H^4 & = & C^{18}H^{12} \\ \text{Diphenyl.} & & \text{Benzene.} & & \text{Phenylene.} & & \text{Phenylene.} & & \text{Chrysene.} \end{array}$$

Passed together with ethylene through a red-hot tube, it is partly converted into cinnamene and benzene: $C^{12}H^{10} + C^2H^4 = C^8H^8 + C^6H^6$; partly into anthracene and hydrogen: $C^{12}H^{10} + C^2H^4 = C^{14}H^{10} + 2H^2$. Heated with 80 pts. of saturated *hydriodic acid*, it is almost wholly converted into hexane: $C^{12}H^{10} + 18HI = 2C^6H^{14} + 9I^2$; with 20 pts. of the acid, partly ($\frac{2}{3}$) into benzene: $C^{12}H^{10} + 2HI = 2C^6H^6 + I^2$; partly ($\frac{1}{3}$) into propane and carbon: $C^{12}H^{10} = C^3H^8 + C^9 + H^2$ (Berthelot, p. 741).

PHENYL CARBONATE. $CO^3(C^6H^5)^2$.—Obtained by heating 3 pts. phenol with 2 pts. liquid phosgene to 140°–150° in a sealed tube. By heating the product with dilute soda-ley, a solid compound is obtained, which crystallises from hot alcohol in white needles having a silky lustre. It is insoluble in water, soluble in alcohol and ether, melts at 78°, gives off a pleasant aromatic odour when heated, and sublimes in long needles. By strong soda-ley, or more easily by alcoholic potash, it is resolved into carbonate and phenylate of sodium. Heated with strong sulphuric acid, it gives off carbon dioxide (Kemp, *Zeitschr. f. Chem.* [2] vi. 205).

PHENYL PHOSPHATES. According to Glutz (*Ann. Ch. Pharm.* cxliii. 181), the *triphenylic phosphate*, $PO^4(C^6H^5)^3$, obtained by treating phenol with phosphorus pentachloride, washing the residue with soda-ley and water, and dissolving in ether, crystallises from the latter by spontaneous evaporation as a coherent mass, consisting of transparent needles, snow-white and inodorous after drying over sulphuric acid. It melts at the heat of the water-bath, is insoluble in water, very easily soluble in alcohol, ether, and hot strong sulphuric acid, and crystallises from the latter in long needles having a silky lustre. By treatment with excess of potash or other strong bases, it is converted into diphenyl-phosphoric acid and phenol:

$$PO^4(C^6H^5)^3 + K^2O = PO^4(C^6H^5)^2K + C^6H^5OK.$$

Diphenyl-phosphoric acid is separated from its potassium salt by hydrochloric acid, as a brown oil slightly soluble in water, easily in alcohol and ether. Its silver salt, $PO^4(C^6H^5)^2Ag$, crystallises in silky needles permanent in the air.

Triphenylic phosphate heated with bromine to 180° yields *bromophenylic orthophosphate*, which, after the crude product has been treated with dilute alkali, crystallises from hot alcohol in nacreous scales:

$$PO^4(C^6H^5)^3 + Br^6 = 3HBr + PO^4(C^6H^4Br)^3.$$

with 120 c. c. of 70 p. c. alcohol; the mixture is introduced into a glass vessel and repeatedly agitated, after the weight has been made up, if necessary, to 125 grams; the liquid is filtered after a while; and 80 c. c. of the filtrate (containing 10 grm. opium) are introduced into a wide stoppered glass. Two grams of the ammoniacal liquid are then transferred by means of a drawn-out pipette to the bottom of the vessel, and the stopper is introduced without allowing the two liquids to mix. After 36 hours the morphine is found separated in thick reddish crystals, the narcotine in slender white needles; the two alkaloïds are separated by levigation, and the morphine is washed with boiling water. Stronger or weaker spirit is not so well adapted for the separation. As, however, a considerable quantity of morphine remains dissolved in the 70 p. c. alcohol (¼ of the whole amount, according to Guilliermond), the results obtained by this process are not absolute, but only comparable under similar conditions.

3. Schachtrupp (*Zeitschr. anal. Chem.* vii. 284, 509) describes a method founded on the solubility of narcotine and the insolubility of morphine in benzol, and the easy solubility of morphine in amylic alcohol. A weighed quantity of opium is treated with a solution of sodium carbonate till the opium is completely comminuted; the still alkaline mixture is evaporated over the water-bath; the dry dusty residue is digested several times with hot benzene; the filter through which the liquid has passed is added to the residue; the remainder of the benzene is evaporated off; and the residue is exhausted with boiling amylic alcohol. The greater part of the morphine then crystallises from the united extracts on cooling. The amylic alcohol is decanted and the greater part of it distilled off; the brown residue is agitated while still hot with water containing hydrochloric acid; the crystals previously obtained are dissolved in the same liquid; and the solution is evaporated to twice the weight of the opium used, then filtered, and precipitated with ammonia. The morphine thus separated, which is still coloured, but otherwise pure, is collected after 24 hours, washed, dried, and weighed. Two samples of Smyrna opium thus treated yielded 8·30 and 8·29 p. c. morphine; the same samples treated by Merck's process gave respectively 7·96 and 8·01 p. c.

For the preparation of morphine also, Schachtrupp recommends the treatment of opium with sodium carbonate, and preliminary exhaustion of the dried mass with hot benzene. The residue again dried is drenched with water; strong acetic acid is added; the mixture warmed for some time and strained; and the undissolved portion is treated several times in the same manner. The united extracts evaporated down to twice the weight of the opium used are mixed with a slight excess of ammonia, and the morphine which separates after some time is redissolved in acetic acid and precipitated by ammonia. For final purification it is dissolved in boiling amylic alcohol, from which it separates in colourless crystals without the use of animal charcoal.

Derivatives of Morphine.

Apomorphine or **Apomorphia.** $C^{17}H^{17}NO^2$ (Matthiessen a. Wright, *Proc. Roy. Soc.* xvii. 455, 460).—An organic base differing from morphine by containing H^2O less, and produced: 1. By heating morphine in a sealed tube to 140°–150° for two or three hours with a large excess of hydrochloric acid:

$$C^{17}H^{19}NO^3 = H^2O + C^{17}H^{17}NO^2.$$

2. From codeine (which has the composition of methyl-morphine) by similar treatment:

$$\underset{\text{Codeine.}}{C^{18}H^{21}NO^3} + HCl = \underset{\text{Methyl-chloride.}}{CH^3Cl} + H^2O + \underset{\text{Apomorphine.}}{C^{17}H^{17}NO^2}$$

The methyl chloride formed in the second case collects on cooling on the top of the tarry contents of the tube, and escapes as gas when the tube is opened. The residue in this or in the first process contains the hydrochloride of apomorphine, and when dissolved in water, and precipitated by sodium carbonate, yields, on extraction with ether and agitation with hydrochloric acid, crystalline hydrochloride of apomorphine, from which the base may be precipitated by sodium bicarbonate, as a snow-white crystalline mass, which quickly turns green on exposure to the air. The green mass is partly soluble in water, communicating to it a fine emerald colour, in alcohol with green, in ether and benzene with splendid rose-purple, and in chloroform with violet colour.

Hydrochloride of apomorphine may also be prepared by digesting morphine with

Chlorophenyl Oxysulphide, $C^{12}H^8Cl^2S^2O^2$, is produced, like phenyl oxysulphide, by heating chlorophenylsulphurous hydride with water to 130°–140°:

$$\begin{array}{ccccccc} 3C^6H^4ClSO^2H & = & C^{12}H^8Cl^2S^2O^2 & + & C^6H^4ClSO^3H & + & H^2O. \\ \text{Chlorophenyl-} & & \text{Chlorophenyl} & & \text{Chlorophenyl-} & & \\ \text{sulphurous hydride.} & & \text{oxysulphide.} & & \text{sulphurous acid.} & & \end{array}$$

It is insoluble in water and alkalis, easily soluble in ether, benzol, and hot alcohol; crystallises from the latter in vitreous four-sided rhombic prisms; melts at 136°–138°, dissolves with indigo colour in fuming sulphuric acid, and is converted by zinc and sulphuric acid into chlorophenyl sulphydrate (Otto, *Ann. Ch. Pharm.* cxlv. 317; *Jahresb.* 1867, p. 629).

PHENYL-ACETYLENE. Syn. with Acetenyl-benzene (p. 5).

PHENYLACRYLIC ACID. Syn. with Cinnamic Acid (p. 467).

PHENYLAMINE or **ANILINE.** $C^6H^5NH^2$.—On the preparation of this base on the manufacturing scale, and on the manufacture and properties of aniline colours, see the article Aniline in this volume.

Reactions.—1. Aniline treated in very dilute solution with *potassium permanganate* is oxidised to hydrazobenzene, $C^{12}H^{12}N^2$, azobenzene, $C^{12}H^{10}N^2$, and azoxybenzene, $C^{12}H^{10}N^2O$ (Glaser, pp. 269–272).—2. Heated with 20 pts. of saturated aqueous *hydriodic acid*, it yields ammonia and benzene; methylaniline similarly treated yields methane and hexane, together with ammonia; ethylaniline yields ethane and hexane; amylaniline yields quintane and hexane (Berthelot).—3. When a dilute aqueous solution of an aniline salt is mixed with *iodine chloride* containing a slight excess of iodine, two oxidised compounds are formed, one soluble in carbon bisulphide, and forming shining crystals several inches long, while the other, which is formed in smaller quantity, is insoluble in carbon bisulphide, and crystallises in reddish scales (Stenhouse, *Chem. Soc. J.* [2] ii. 327).

4. Aniline well cooled and added by drops to *phosphorus trichloride*, is converted into the hydrochloride of phosphaniline, $C^{18}H^{18}PN^3.3HCl$ (Tait, *Zeitschr. f. Chem.* [2] 648). (See Phosphaniline, p. 932.)—5. When 3 pts. aniline are heated to 145° with 1 pt. *chloropicrin*, nitrogen is abundantly evolved, and the residue yields to water a red colouring matter, together with hydrochloride of carbotriphenyltriamine, $C^{iv}(C^6H^5)^3H^2N^3$ (Basset, *Chem. Soc. J.* [2] iii. 21).—6. A mixture of 2 mol. aniline and 1 mol. *chlorotoluene* heated to 160° for 24 hours yields aniline hydrochloride, together with a base isomeric with phenyl-tolylamine (Fleischer, *Ann. Ch. Pharm.* cxxxviii. 225):

$$2C^6H^7N + C^7H^7Cl = C^6H^7N.HCl + C^{13}H^{13}N.$$

7. Aniline in excess heated with *ethyl monochloracetate* and water in a sealed tube to 180°–140°, is converted into anilido-acetanilide, together with alcohol and aniline hydrochloride (Wilm a. Wischin, *Zeitschr. f. Chem.* [2] iv. 75):

$$\begin{array}{ccccccccc} \begin{array}{l} CH^2Cl \\ | \\ COOC^2H^5 \end{array} & + & 3(C^6H^5.H^2N) & = & C^2H^5OH & + & C^6H^5NH^2.HCl & + & \begin{array}{l} CH^2NH(C^6H^5) \\ | \\ CONHC^6H^5 \end{array} \\ \text{Ethyl chlor-} & & \text{Aniline.} & & \text{Alcohol.} & & \text{Aniline hydro-} & & \text{Anilido-acetanilide.} \\ \text{acetate.} & & & & & & \text{chloride.} & & \end{array}$$

8. On the action of *glycolic chlorhydrin* on aniline, see Wurtz (*Zeitschr. f. Chem.* [2] v. 482).—9. Aniline heated with *hydrochloric acid* and *potassium ferrocyanide* is converted into a red colouring matter called lydine (Guyot, p. 793).

10. Aniline unites with *sulphurous oxide* (as described by Hofmann), apparently forming the compound $C^6H^7N.SO^2$, or perhaps $\left.\begin{array}{c} C^6H^5 \\ (SO)'' \\ H^2 \end{array}\right\}\begin{array}{c} N \\ O \end{array}$, which when exposed to the air gives off a large quantity of sulphurous oxide, leaving the compound $2C^6H^7N.SO^2$; and this when suspended in ether, again takes up sulphurous oxide. *Acetic aldehyde* acts violently on the compound $C^6H^7N.SO^2$, forming a brown viscid mass chiefly consisting of diethylidene-diphenylamine. In ethereal solution colourless prisms are formed, consisting of $C^6H^7N.C^2H^4O.SO^2$, insoluble in ether, slightly soluble in cold water, easily in alcohol, and decomposed by heat, with formation of *diethylidene-diphenyl-diamine* (iv. 457), which is easily prepared in this manner:

$$2(C^6H^7N.C^2H^4O.SO^2) = \left.\begin{array}{c} (C^2H^4)^2 \\ (C^6H^5)^2 \end{array}\right\}N^2 + 2SO^2 + 2H^2O.$$

Œnanthol and *bitter almond oil* act less energetically, forming the compounds

$2C^6H^7N.2C^7H^{14}O.SO^2$ and $2C^6H^7N.2C^7H^6O.SO^2$. The more easily decomposible valeral compound seems to have a similar constitution (Schiff, *Ann. Ch. Pharm.* cxl. 92).

11. On the action of *aldehydes* on aniline, see DIPHENYLDIAMINES (iv. 456, and p. 79 of this volume).

12. On the action of the *camphene hydrochlorides*, $C^{10}H^{16}.HCl$ and $C^{10}H^{16}.2HCl$, on aniline, see TEREBENES.

Bromophenylamines.—Mono- and di-bromaniline are formed, as well as tribromaniline, by the direct action of bromine on aniline, namely, by passing bromine-vapour mixed with air into aniline, or by gradually adding a solution of bromine in benzol to aniline also dissolved in benzol (Kekulé, *Zeitschr. f. Chem.* [2] ii. 667). Di- and tri-bromaniline are also produced by heating nitrobenzene to 185°–190° in sealed tubes with fuming hydrobromic acid, the nitrobenzene being first reduced to aniline, according to the equation:

$$C^6H^5NO^2 + 6HBr = C^6H^5NH^2 + 3Br^2 + 2H^2O,$$

and the free bromine then acting upon the aniline as above (Baumhauer, *Zeitschr. f. Chem.* [2] v. 198).

Trichloraniline, $C^6H^4Cl^3N$, is formed by the action of tin and hydrochloric acid on trichloronitrobenzene in alcoholic solution: $C^6H^2Cl^3(NO^2) + 3H^2 = 2H^2O + C^6H^4Cl^3N$. By dissolving the crystalline compound which separates on cooling in alcohol, freeing it from tin by hydrogen sulphide, and evaporating the filtrate, trichloraniline is obtained in long shining needles slightly soluble in cold, more soluble in hot water, also in alcohol, ether, benzol, moderately dilute mineral acids, and strong caustic potash. With strong sulphuric acid it forms a rose-coloured solution, from which the trichloraniline may be distilled without alteration. It melts at 96·5°, solidifies at 86°, and boils near 270°. The aqueous solution forms with chloride of lime or chromic acid a dye of the colour of vermillion. The solution in strong sulphuric acid becomes bluish-violet on addition of a little nitric acid, and then reddish-yellow when warmed or mixed with water. The vapour passed over red-hot lime yields ammonia and aniline (Lesimple, *Ann. Ch. Pharm.* cxxxvii. 125).

Iodaniline, C^6H^6IN, exhibits two modifications, α and β, obtained from the corresponding modifications of diazonitrobenzene:

$$\underset{\substack{\text{Diazonitro-}\\\text{benzene.}}}{C^6H^3(NO^2)N^2} + HI = \underset{\substack{\text{Iodonitro-}\\\text{benzene.}}}{C^6H^4(NO^2)I} + N^2$$

$$\underset{\substack{\text{Iodonitro-}\\\text{benzene.}}}{C^6H^4(NO^2)I} + 3H^2 = \underset{\text{Iodaniline.}}{C^6H^4I.NH^2} + 2H^2O.$$

An aqueous solution of α diazonitrobenzene nitrate mixed with hydriodic acid yields α iodonitrobenzene, crystallising in yellow needles, melting at 171·5°, and identical with that which is obtained by the action of nitric acid on iodobenzene, and this compound treated with ammonium sulphide is converted into α iodaniline melting at 60°, and identical with that which Hofmann obtained by the action of iodine on aniline (iv. 444). β Iodonitrobenzene, obtained in like manner from β diazonitrobenzene, is converted by ammonium sulphide into β iodaniline or para-iodaniline, crystallising in silvery laminæ, and melting at 25°.

The melting points of α iodaniline and of all the benzene-derivatives of the same series are higher than those of the corresponding compounds of the β or para- series; thus:

	α	β
Iodonitrobenzene	171·5°	34°
Bromonitrobenzene	120°	56°
Chloronitrobenzene	83°	46°
Nitraniline*	141°	108°
Iodaniline	60°	25°
Bromaniline	57°	liquid at ord. temp.
Chloraniline	64°	„ „
Diazo-amidonitrobenzene	245°	195°
Diazo-nitrobenzolimide	71°	53°

(Griess, *Chem. Soc. J.* [2] v. 857; *Jahresb.* 1866, p. 457).

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* The prefixes α and β are here applied to the nitranilines in the opposite sense to that attached to them in vol. iv. p. 446, β or para-nitraniline being the modification obtained by reduction of dinitrobenzene.

β Nitraniline treated in alcoholic solution with sodium-amalgam is converted into hydrazoaniline, $C^{12}H^{14}N^4$ (Harrhaus, p. 703).

Diphenylamine. $(C^6H^5)^2HN$.—This base, discovered by Hofmann (iv. 453) amongst the products of the dry distillation of aniline-blue, is likewise formed by the action of aniline on various aniline salts, according to the equation: $C^6H^5.H^2N + C^6H^5.H^2N = (C^6H^5)^2HN + NH^3$. It may be prepared by heating 1½ mol. aniline with 1 mol. aniline hydrochloride to 210°–214° for thirty to thirty-five hours in a long-necked flask provided with a condensing tube, or more quickly by heating the same mixture in a closed vessel under a pressure of four or five atmospheres. On treating the product—which is a mixture of diphenylamine hydrochloride, aniline hydrochloride, and colouring matters—with hot hydrochloric acid diluted with 20 to 30 times its bulk of water, the diphenylamine hydrochloride is decomposed by the water, and the base thus separated rises to the surface as an oil which solidifies on cooling: it is purified by repeated crystallisation from ether or benzol, in which the colouring matters are insoluble, and finally by distillation. It then forms a white substance which boils at 310° (De Laire, Girard, a. Chapoteant, *Bull. Soc. Chim.* [2] vii. 360).

Phenyl-diamines (Hofmann, *Proc. Roy. Soc.* xv. 55).—Diamines containing 2 atoms of phenyl and 1 atom of a trivalent alcohol-radicle, such as methenyl, ethenyl, &c. are produced by the action of phosphorus trichloride on a mixture of aniline with a fatty acid, acid chloride, or anilide, *e.g.* ethenyl-diphenyl-diamine, $(C^2H^3)'''(C^6H^5)^2HN^2$, by the action of PCl^3 on a mixture of aniline with acetic acid, acetyl chloride, or phenyl-acetamide. The phenyl-diamines containing ethenyl are described under ETHENYL-DIAMINES (p. 585). *Methenyl-diphenyl-diamine*, $(CH)'''(C^6H^5)^2HN^2$, is described as formyl-diphenyl-diamine in vol. iv. p. 459.

Quintenyl-diphenyl-diamine, $C^{17}H^{20}N^2 = \left.\begin{matrix}(C^5H^9)''' \\ (C^6H^5)^2 \\ H\end{matrix}\right\}N^2$, is obtained by heating 3 mol. valeric acid and 6 mol. aniline with 2 mol. phosphorus trichloride to 150°, precipitating the aqueous solution of the resulting viscid mass with soda-ley, and recrystallising from alcohol. It is nearly insoluble in water, melts at 111°, and forms a platinum salt which crystallises in rhombic tables, slightly soluble in water, nearly insoluble in alcohol.

Benzenyl-diphenyl-diamine, $C^{19}H^{16}N^2 = \left.\begin{matrix}(C^7H^5)''' \\ (C^6H^5)^2 \\ H\end{matrix}\right\}N^2$, obtained in like manner with 3 mol. phenyl-benzamide, 3 mol. aniline hydrochloride, and 1 mol. phosphorus trichloride, crystallises in slender silky needles; the hydrochloride in sparingly soluble laminæ, which lose the whole of their acid on recrystallisation.

Phenyl-diamines containing aldehyde-radicles, ethylidene, benzylidene, &c., produced by the action of aldehydes on aniline, have been obtained by Schiff, and several of them are described in vol. iv. pp. 456–459.

Ethylidene-diethyl-diphenyl-diamine, $C^{18}H^{24}N^2 = (C^2H^4)''(C^2H^5)^2(C^6H^5)^2N^2$, produced by the action of acetic aldehyde on ethyl-aniline, is a thick, bitter, scentless liquid, not distillable without decomposition, and forming with the stronger acids, salts which are decomposed by water. The *platinochloride* has the composition $2(C^{18}H^{24}N^2.HCl).PtCl^4$.

Diheptylidene-diphenyl-diamine, $(C^7H^{14})^2(C^6H^5)^2N^2$, previously obtained by the action of œnanthol on aniline, is also produced by heating aniline with œnanthol-sodium sulphite:

$$2(C^7H^{14}O.NaHSO^3) + 2C^6H^7N = \left.\begin{matrix}(\overset{\prime\prime}{C}{}^7H^{14})^2 \\ (C^6H^5)^2\end{matrix}\right\}N^2 + Na^2SO^3 + SO^2 + 3H^2O.$$

The dibenzylidene compound is obtained in a similar manner (Schiff, *Ann. Ch. Pharm.* cxl. 92; *Jahresb.* 1866, p. 440).

PHENYLENE SULPHIDE (Stenhouse, *Proc. Roy. Soc.* xvii. 62; *Ann. Ch. Pharm.* cxlix. 252).—This compound is produced, together with phenylic sulphate and monosulphide, by the dry distillation of sodium phenylsulphite in an iron vessel, and remains after all the products volatile at 300° have passed over. On distilling the dark-coloured residue in a copper retort, an orange-coloured distillate is obtained, which after several days deposits a considerable quantity of large tabular crystals; and these, when freed from adhering oil by draining and pressure between paper, from phenyl bisulphide and other impurities by exhaustion with hot alcohol, and recrystallised from benzol or carbon bisulphide, and finally from alcohol, yield pure phenylene sulphide, in long, colourless, transparent, shining prisms. It is insoluble in water, slightly soluble in cold alcohol (1 pt. in about 400), more soluble in hot alcohol; melts at 159°, and resolidifies at 153°. It dissolves in strong sulphuric acid, forming a liquid of a splendid purple colour, and becoming red with a purple tinge when mixed with a considerable quantity of the concentrated acid; on addition of water this colour disappears, and a crystalline precipitate separates, which appears to consist of unaltered phenylene sulphide. With strong nitric acid it yields a crystalline substance, probably a nitro-substitution product.

PHENYLENE SULPHOBROMIDE, $C^6H^4SBr^2$, is produced by the action of bromine-vapour on phenylene sulphide, or more easily by adding bromine in slight excess to a cold-saturated solution of the sulphide in anhydrous carbon bisulphide, the compound then separating in small black prisms, which may be purified by washing with cold carbon bisulphide, and freed from that liquid by placing them under an air-pump receiver, exhausting, readmitting the air, and repeating these operations several times. The sulphobromide slowly gives up its bromine when exposed to dry air, and is quickly decomposed by moisture, with evolution of hydrobromic acid. It is moderately soluble in carbon bisulphide and in carbon tetrachloride (Stenhouse, *loc. cit.*).

PHENYLENE-DIAMINE. $C^6H^8N^2 = \left.\begin{matrix}(C^6H^4)'' \\ H^4\end{matrix}\right\}N^2$ (iv. 480).—The hydriodides of α and β phenylene-diamine are formed by the action of hydriodic acid on the corresponding nitranilines, the reduction of the α nitraniline appearing to require a somewhat higher temperature than that of β nitraniline. The α hydriodide is easily soluble, and crystallises in indistinct laminæ; the β salt is but slightly soluble, and crystallises in broad micaceous rectangular tables (Mills, *Chem. Soc. J.* [2] ii. 152).

Beta- or para-phenylene-diamine is formed, together with aniline, by heating amidazobenzene with tin and hydrochloric acid (Martius a. Griess, *Jahresb.* 1865, p. 419):

$$C^{12}H^9(NH^2)N^2 + 2H^2 = C^6H^8N^2 + C^6H^7N.$$

A double salt of phenylene-diamine hydrochloride and stannous chloride, $C^6H^8N^2.2HCl.2SnCl^2$, is formed by treating a mixture of dinitrobenzene (1 mol.) and metallic tin (6 at.) with strong hydrochloric acid. The whole dissolves with violent action, and the solution when left to evaporate deposits the double salt in needles having a silky lustre (H. Gerdemann, *Zeitschr. f. Chem.* [2] i. 51).

When nitrous acid is passed into the aqueous solution of phenylene-diamine hydrochloride, nitrogen is evolved, and a dark violet body, $C^{12}H^{10}N^4O^3$, is formed, slightly soluble in water, alcohol, and ether. This body slowly gives off nitrogen when treated with hydrochloric acid, and yields aniline hydrochloride when boiled with tin and hydrochloric acid. An acidulated solution of phenylene-diamine hydrochloride gives with potassium nitrite a brown amorphous precipitate (Hollemann, *ibid.* 555).

Dibromophenylene-diamine, $C^6H^6Br^2N^2$, is obtained as a dark brown precipitate on mixing the hydrochloride of phenylene-diamine with bromine till the odour of the latter remains permanent after some hours. It is nearly insoluble in ether, but dissolves easily in alcohol, and crystallises therefrom; cannot be sublimed without decomposition (Hollemann).

PHENYL-HYPOSULPHUROUS ACID. $C^6H^6S^2O^3$ (Stenhouse, *Proc. Roy. Soc.* xvii. 62; *Ann. Ch. Pharm.* cxlix. 254).—This acid is formed by dissolving phenyl sulphide $(C^6H^5)^2S$, with aid of heat in strong sulphuric acid. On dissolving the semi-solid mass which forms on cooling in a large quantity of water, neutralising with barium carbonate, evaporating the filtrate till a crystalline film forms on its surface, and then leaving it to cool, *barium phenylhyposulphite*, $(C^6H^5S^2O^3)^2Ba + 2H^2O$, separates in crusts composed of microscopic crystals. The copper salt also forms crystalline crusts. The calcium and sodium salts do not crystallise so well as the barium salt.

PHENYL-SULPHURIC ACID. $C^6H^6SO^4$ (Kekulé, *Zeitschr. f. Chem.* [2] iii. 641; *Jahresb.* 1867, p. 637).—Two modifications of this acid, which may be distinguished as α and β, are produced by dissolving phenol at a gentle heat in an equal weight of strong sulphuric acid; on diluting the product with water, neutralising with lead carbonate, decomposing the lead salts with hydrogen sulphide, neutralising the acid filtrate with potassium carbonate, and evaporating, potassium α phenylsulphate crystallises out first in six-sided anhydrous laminæ, while the β phenylsulphate is obtained from the mother-liquor in needles containing 2 mol. water. These two potassium salts, when fused with excess of potash, yield different modifications of oxyphenol, $C^6H^6O^2$, the α salt yielding resorcin, and the β salt pyrocatechin:

$$C^6H^5SO^4K + KHO = SO^4K^2 + C^6H^6O^2.$$

From this it would appear that the α and β phenylsulphuric acids both have the constitution $C^6H^4\left\{\begin{matrix}OH\\SO^3H\end{matrix}\right.$, and differ only in the relative positions of the radicles OH and SO^3H; in fact, that the α acid is paraphenylsulphuric acid (1, 4), and the β acid metaphenylsulphuric acid (1, 3). But from the different reactions of the α and β potassium salts with benzoyl chloride (p. 925), the two acids appear rather to be related to one another in the same manner as isethionic and ethylsulphuric acids; thus:

$$\begin{array}{cc} C^2H^4\left\{\begin{matrix}OH\\SO^3H\end{matrix}\right. & O\left\{\begin{matrix}C^2H^5\\SO^3H\end{matrix}\right. \\ \text{Isethionic.} & \text{Ethylsulphuric.} \\ C^6H^4\left\{\begin{matrix}OH\\SO^3H\end{matrix}\right. & O\left\{\begin{matrix}C^6H^5\\SO^3H\end{matrix}\right. \\ \alpha\ \text{Phenylsulphuric.} & \beta\ \text{Phenylsulphuric.} \end{array}$$

A third modification, γ *phenylsulphuric acid*, has been shown by Solommanoff (*Zeitschr. f. Chem.* [2] v. 294) to be formed, simultaneously with the α and β acids, by the action of sulphuric acid on phenol, its potassium salt being obtained in small quantity from the last mother-liquors of the β potassium salt.

α *Phenylsulphate of potassium* melts at 240° and decomposes at a higher temperature. Its aqueous solution gives with basic lead acetate a white precipitate of a basic lead salt nearly insoluble in boiling water. *Potassium β phenylsulphate* crystallises with various quantities of water; from boiling water it separates with 1 mol. water; by spontaneous evaporation, with 2 mol. It is efflorescent, and is sharply distinguished from the α and γ salts by its property of melting at 235°-240° to a yellow transparent liquid which solidifies to a vitreous mass on cooling. Its aqueous solution gives with basic lead acetate a white precipitate of a basic β phenylsulphate of lead, which cakes together when the liquid is boiled, is dissolved by boiling water, and separates out as a white powder on cooling. The γ *potassium salt* crystallises in thin plates and needles, and is very soluble in water; the crystals contain about 2½ mol. water, and do not effloresce quite so quickly as those of the β salt; they do not melt at 240°. With basic lead acetate this salt gives a white precipitate which does not cake together on heating the liquid, and is but slightly dissolved by boiling water (Solommanoff).

The α potassium salt is obtained at once in the pure state by digesting 1 mol. phenol at a gentle heat with 1 mol. chlorhydric sulphate, SO^3HCl, neutralising the aqueous solution of the product with barium carbonate, and decomposing the resulting barium salt with potassium carbonate. When 1 mol. SO^3HCl is digested with 2 mol. phenol, and the aqueous solution of the product is agitated with ether to remove unaltered phenol, then neutralised with potassium carbonate and evaporated, the solution first deposits laminæ of the α potassium salt, and the mother-liquor yields needles of the β salt. The dry α potassium salt treated with chlorhydric sulphate is converted into potassium phenyl-disulphate, $C^6H^3OH(SO^3K)^2$ (Solommanoff).

Several salts of phenylsulphuric acid (α ?) have been examined by Menzner (*Ann. Ch. Pharm.* cxliii. 75; *Jahresb.* 1867, p. 641).

Chlorophenyl-sulphuric acid, $C^6H^4Cl.SO^4H$, is formed by mixing 200 grms. monochlorophenol with 150 grms. fuming sulphuric acid. On leaving the crystallising mass to itself for some days, then converting it into a barium salt, and the latter into a potassium salt, the anhydrous salt $C^6H^4Cl.SO^4K$ separated out first in stellate groups of short flat prisms; then the hydrated salt $C^6H^4Cl.SO^4K + 2H^2O$, in flat colourless monoclinic crystals, often united in crosses. This salt gives off its water at 110°, melts at 245°, and decomposes with intumescence at 300°. The mother-liquor contained considerable quantities of very soluble salts (Bähr-Predari, *Zeitschr. f. Chem.* [2] vi. 246).

Dichlorophenylsulphuric acid, $C^6H^3Cl^2.SO^4H$, is produced as a potassium salt by stirring up a mixture of 10 pts. of potassium phenylsulphate (α) and 3 pts. potassium chlorate with 22 pts. commercial hydrochloric acid, the mixture being cooled, if necessary, to moderate the action. The resulting pasty mass washed with alcohol and ether to remove chlorophenols, and recrystallised from hot water, yields the potassium salt, $C^6H^3Cl^2SO^4K$, in white shining scales, easily soluble in hot, less soluble in cold water. The acid $C^6H^3Cl^2SO^4H$, prepared by decomposing this salt with an equivalent quantity of dilute sulphuric acid, evaporating to dryness, exhausting the residue with absolute alcohol, and evaporating the alcoholic solution, finally in a vacuum over sulphuric acid, crystallises in colourless very deliquescent rhombic tables or prisms. The *barium salt*, $C^6H^3Cl^2SO^4Ba + 2H^2O$ (at 100°), separates by evaporation in white crystalline crusts (Kolbe a. Gauhe, *Ann. Ch. Pharm.* cxlvii. 71; *Zeitschr. f. Chem.* [2] v. 232).

On the chlorophenylsulphuric acids, see, further, Petersen a. Bähr-Predari (*Ann. Ch. Pharm.* [1871] clxvii. 121–165; *Chem. Soc. J.* [2] ix. 240).

Nitrophenylsulphuric Acid. $C^6H^4(NO^2)SO^4H$.—The potassium salt of this acid is obtained by heating a mixture of 1 pt. finely pulverised potassium phenol-sulphate (*a*) and 1 pt. nitre with 1 pt. strong sulphuric acid and 5 pts. water, and purified in the same manner as the dichlorophenylsulphate. When decomposed by dilute sulphuric acid, it yields nitrophenolsulphuric acid, which crystallises from alcohol by evaporation, finally in a vacuum, in colourless, short, whetstone-shaped, very deliquescent crystals. Ammonium sulphide converts it into a difficultly crystallisable substance, probably the corresponding amido-acid.

Nitrophenylsulphuric acid forms salts containing 1 and 2 at. metal. The *potassium salt*, $C^6H^4(NO^2)SO^4K$, crystallises in stellate groups of needles; the *ammonium salt*, $C^6H^3(NO^2)SO^4(NH^4)^2$, in brownish-yellow prisms. The *barium salt*, $C^6H^3(NO^2)SO^4Ba$, forms small indistinct orange-red crystals, which retain 2 mol. crystallisation-water at 100°, and become anhydrous at 170°–180°. The *cupric salt*, $[C^6H^4(NO^2)SO^4]^2Cu$, is a yellow-green indistinctly crystalline mass. The *lead salt*, $[C^6H^4(NO^2)SO^4]^2Pb$, crystallises in short thick yellow needles, easily becoming basic by evaporation (Kolbe a. Gauhe).

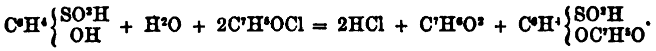
Kekulé (*Zeitschr. f. Chem.* [2] v. 602) has obtained the same acid by the action of sulphuric acid on the volatile modification of nitrophenol.

Benzoyl-phenylsulphuric Acid. $C^6H^4(C^7H^5O)SO^4H = C^6H^4\left\{\begin{matrix}SO^3H\\OC^7H^5O\end{matrix}\right.$ (Engelhardt a. Latschinoff, *Zeitschr. f. Chem.* [2] iv. 75).—This acid is produced: 1. As a potassium salt by heating the potassium salt of *a* phenylsulphuric acid with benzoyl chloride for some hours to 140°–150°. The chlorine then acts on the hydrogen of the water-residue in the phenol, forming hydrochloric acid, and the benzoyl takes the place of the hydrogen removed; thus:

$$C^6H^4(OH)SO^3K + C^7H^5OCl = HCl + C^6H^4(OC^7H^5O)SO^3K.$$

The dry white residue washed with ether to remove admixed benzoyl chloride and benzoic acid, and recrystallised from boiling water, yields needle-shaped crystals of potassium benzoyl-phenylsulphate.

2. By treating 1 mol. phenyl-sulphuric acid (formed from C^6H^6O and SO^4H^2) with 2 mol. benzoyl chloride. The reaction is as follows:



$$C^6H^4\left\{\begin{matrix}SO^3H\\OH\end{matrix}\right. + H^2O + 2C^7H^5OCl = 2HCl + C^7H^6O^2 + C^6H^4\left\{\begin{matrix}SO^3H\\OC^7H^5O\end{matrix}\right..$$

The reaction is assisted by a gentle heat; and the product is treated with cold water, which extracts the benzoyl-phenylsulphuric acid, and leaves benzoic acid, phenyl benzoate, and an indifferent oil resulting from the action of the benzoyl chloride on the *β* phenylsulphuric acid present. On saturating the aqueous solution with barium carbonate, the sparingly soluble benzoyl-phenylsulphate of barium is deposited, while an easily soluble not isomeric salt remains in the mother-liquor.

3. By the action of sulphuric anhydride on phenyl benzoate cooled with snow:

$$C^6H^5OC^7H^5O + SO^3 = C^6H^4(SO^3H)OC^7H^5O.$$

The quantity of benzoyl-phenylsulphuric acid obtained by this method is however but small, and another acid not yet examined is formed at the same time.

The acid obtained by the second or third process yields a potassium salt exactly agreeing with that obtained by the first process. This acid may therefore be distinguished as *a* benzoyl-phenylsulphuric acid. Its formation in the second process results from the action of the benzoyl chloride on the *a* phenylsulphuric acid present, the *β* acid giving rise to the indifferent oil above mentioned.

Potassium a Benzoyl-phenylsulphate, $C^6H^4(OC^7H^5O)SO^3K$, dissolves easily in boiling, sparingly in cold water, and separates from aqueous solution in long needles; it dissolves also in boiling alcohol, and separates therefrom in flat shining needles. Heated with hydrochloric acid, it decomposes, with separation of benzoic acid; a similar decomposition takes place also when it is digested with potassium carbonate.

The *barium salt*, $[C^6H^4(OC^7H^5O)SO^3]^2Ba$, precipitated from the solution of the potassium salt by barium chloride, is sparingly soluble in cold, nearly insoluble in boiling water, and separates from the hot solution on cooling in tufts of slender needles. The *calcium salt*, $[C^6H^4(OC^7H^5O)SO^3]^2Ca$, resembles the barium salt. The *lead salt*, $[C^6H^4(OC^7H^5O)SO^3]^2Pb + 2H^2O$, dissolves sparingly in cold, more easily in boiling water, and crystallises in nodular tufts of needles. The *magnesium salt* crystallises in shining laminæ slightly soluble in cold, more easily in boiling water. The *copper salt*, $[C^6H^4(OC^7H^5O)SO^3]^2Cu + 6H^2O$, forms shining blue laminæ, which give off water and become colourless when heated. The *silver salt*, $C^6H^4(OC^7H^5O)SO^3Ag$, crystallises in laminæ more soluble in hot than in cold water.

Benzoyl chloride acts upon the potassium salt of γ phenyl-sulphuric acid at 140°, in the same manner as on the α salt, producing potassium γ *benzoyl-phenylsulphate*, which when dried at 130° has the composition $C^6H^4(OC^7H^5O)SO^3K$. It is sparingly soluble in cold, easily in boiling water, and separates as a gelatinous mass consisting of nodular groups of very slender needles. It dissolves also in boiling alcohol, and the solution solidifies on cooling to a gelatinous mass changing spontaneously to stellate groups of needles. The *barium salt*, $[C^6H^4(OC^7H^5O)SO^3]^2Ba$, is less soluble in water than the corresponding α salt, and separates from a boiling solution on cooling, in the form of a white powder (Solommanoff, *Zeitschr. f. Chem.* [2] v. 297).

The potassium salt of β phenylsulphuric acid reacts with benzoyl chloride quite differently from the α and γ salts. The mixture heated to 125° melts, without evolution of hydrochloric acid, to a yellow liquid, which solidifies on cooling to a viscid amorphous mass; and on treating this mass with potash, dissolving the oil thereby separated in ether, and evaporating, a crystalline mass is obtained which, when freed by pressure from a yellow oil and redissolved in alcohol and ether, yields crystals of phenyl-benzoyl or benzophenone, $C^6H^5.C^7H^5O$. This is the only well-characterised product of the reaction. The yellow oil has not been analysed, but it appears to contain sulphur. Only a very small quantity of potassium benzoyl-phenyl-sulphate is obtained, consisting apparently of the γ modification, the formation of which is due to the presence of a small quantity of γ phenyl-sulphate (Solommanoff).

From the reactions above detailed it appears that α and β phenylsulphuric acids are related to one another in the same manner as isethionic and ethyl-sulphuric acids, the α acid being constituted like isethionic acid, $C^2H^4\left\{\begin{matrix}SO^3H\\OH\end{matrix}\right.$, and ethyl-sulphuric acid, $O\left\{\begin{matrix}C^2H^5\\SO^3H\end{matrix}\right.$

The relation of these acids to phenol may be exhibited by the following formulæ:

Phenol,	C^6H^5OH.
Potassium phenate,	C^6H^5OK.
Phenyl benzoate,	$C^6H^5O(C^7H^5O)$.
α Phenyl-sulphuric acid,	$C^6H^4(SO^3H)OH$.
Benzoyl-phenylsulphuric acid,	$C^6H^4(SO^3H)O(C^7H^5O)$.
β Phenylsulphuric acid,	$C^6H^5O(SO^3H)$.
Phenyl-phosphoric acid,	$C^6H^5O(PO^3H^2)$.

The formula of β phenyl-sulphuric acid, which contains no *alcoholic* hydrogen, shows that this acid cannot give rise to an isomeride of the benzoyl-phenylsulphuric acid derived from α phenylsulphuric acid (Engelhardt a. Latschinoff). As α and γ phenol-sulphuric acids both give rise to benzoyl-phenylsulphuric acids, they probably differ only in the relative positions of the groups OH and SO^3H.

Phenyl-disulphuric Acid. $C^6H^6S^2O^7 = C^6H^3\left\{\begin{matrix}SO^3H\\SO^3H\\OH\end{matrix}\right.$ (Kekulé, *Zeitschr. f. Chem.* [2] ii. 693. Engelhardt a. Latschinoff, *ibid.* iv. 270). *Disulphophenylenic Acid* (Griess, *Jahresb.* 1866, p. 466). *Oxyphenylene-disulphonic Acid* (Weinhold, *Ann. Ch. Pharm.* cxliii. 58). *Phenetyldisulphonic Acid* (Städeler, *ibid.* cxliv. 295).—This acid is produced by treating phenylsulphuric acid or phenol with excess of ordinary strong sulphuric acid, or better with a mixture of ordinary and fuming sulphuric acid, or with vapour of sulphuric anhydride, also by the action of strong sulphuric acid on diazobenzene sulphate. Engelhardt a. Latschinoff heat 100 grms. phenol on the water-bath with 400 grms. of a mixture of equal parts of ordinary and fuming sulphuric acid. On diluting the product with water, nearly saturating it with barium carbonate, and concentrating the slightly acid filtrate, an abundant crystallisation of barium phenyldisulphate is obtained, which may be purified by recrystallisation from water.

Phenyl-disulphuric acid separated from its lead or barium salt, and evaporated over sulphuric acid, crystallises at first in long silky needles, and then solidifies to a very deliquescent crystalline mass (Städeler). According to Weinhold, the solution

Trichloronaphthalene, $C^{10}H^5Cl^3$, obtained by boiling chloronaphthalene tetrachloride with alcoholic potash, crystallises from ether-alcohol in brittle prisms melting at 81°. Its nitro-product is a soft, yellow, crystalline mass.

Heptachlorodinaphthalene, $C^{20}H^9Cl^7 = C^{10}H^5Cl^3 . C^{10}H^4Cl^4$ (?), crystallises from ether-alcohol in very long, yellowish, waxy needles melting at 106°. By prolonged boiling with alcoholic potash it is converted into a product which crystallises from ether-alcohol in colourless six-sided prisms melting at 101°–102°. *Heptachlorodinitrodinaphthalene*, $C^{20}H^7Cl^7(NO^2)^2$ (= $C^{10}Cl^4Cl^3NO^2 . C^{10}H^3Cl^4NO^2$?), crystallises from alcohol in soft yellowish needles melting at 104°–106°.

Tetrachloronaphthalene, $C^{10}H^4Cl^4$, exists also in two isomeric forms: *α*. Produced by boiling dichloronaphthalene tetrachloride with alcoholic potash. Crystallises from ligroïn and ether in soft white needles which melt at 130°. Its nitro-product forms yellow crystalline nodules.—*β*. Forms, as above mentioned, the ultimate product of the action of chlorine gas on heated chloronaphthalenes. It is originally obtained in long yellow needles, but after repeated crystallisation from alcohol, forms soft white needles which melt at 156°–158°. The nitro-product is a soft yellow mass.

All the chloronaphthalenes are easily soluble in ether, ligroïn, and chloroform, less easily in alcohol; they have an odour of naphthalene, weaker as their amount of chlorine is greater, and in the tetrachloronaphthalenes scarcely perceptible. Their nitro-derivatives are mostly soft yellow masses which are difficult to purify, and when heated with aqueous soda or ammonia, are partly converted into a brown-red colouring matter (Faust a. Saame).

Pentachloronaphthalene, $C^{10}H^3Cl^5$, is produced by heating 1 mol. dichloronaphthoquinone with 2 mol. phosphorus pentachloride to 180°–200° in a sealed tube till the yellow crystals disappear:

$$C^{10}H^4Cl^2O^2 + 2PCl^5 = HCl + 2POCl^3 + C^{10}H^3Cl^5.$$

On washing the product with water and dilute soda-ley, and distilling, the pentachloronaphthalene passes over at a temperature above the boiling point of mercury, solidifies in the receiver, and may be obtained in colourless needles by recrystallisation from alcohol. It is insoluble in water, slightly soluble in cold, more freely in hot alcohol, easily soluble in ether. It melts at 108·5°, may be sublimed in needles by cautious heating, and distils unaltered at a higher temperature. It is not attacked by alkalis. It is much less easily oxidable than naphthalene, not being attacked by chromic acid mixture, or by boiling nitric acid of sp. gr. 1·35. By the action of fuming nitric acid, and more easily by heating it in sealed tubes to 180°–200° with nitric acid of sp. gr. 1·15 to 1·2, it is converted into tetrachlorophthalic acid, $C^8H^4Cl^2O^4$ (Graebe, *Ann. Ch. Pharm.* clxix. 8).

Octochloro- or *Perchloro-naphthalene.* $C^{10}Cl^8$.—Berthelot a. Jungfleisch (*Ann. Ch. Phys.* [4] xv. 332) have prepared this compound—first obtained by Laurent (iv. 13)—by treating naphthalene with chlorine, ultimately with addition of antimonic chloride. The product, sublimed and recrystallised from carbon bisulphide, exhibits properties different from those assigned to it by Laurent. It forms splendid crystals belonging to the rhombic system, melts at 135°, and boils with slight decomposition at 403°; 20 c. c. of its solution in carbon bisulphide saturated at 15° contained 5·86 grm. of the compound. Heated with potassium hydrate, it gives off violet vapours (according to Laurent it is not attacked). Heated with hydriodic acid it yields the same products as naphthalene. Its vapour passed, together with hydrogen, through a red-hot tube yields, together with naphthalene, chiefly resinous and coloured products similar to those produced under the same circumstances from naphthalene.

Cyanonaphthalenes. *Monocyano-naphthalene* or *Naphthyl Cyanide*, $C^{10}H^7CN$, is obtained in two modifications, *α* and *β*, by heating the potassium salts of the corresponding naphthyl-sulphurous acids with potassium cyanide:

$$C^{10}H^7.SO^3K + CNK = SO^3K^2 + C^{10}H^7(CN).$$

The *α cyanide* distils over at about 300°, and after a few rectifications forms a colourless liquid having an agreeable odour somewhat like that of bitter almond oil, a sharp burning taste, and solidifying in a few days at ordinary temperatures, quickly and completely at 0°. It may be easily purified by crystallisation from ligroïn, from which it separates in splendid groups of needles having a satiny lustre. It melts constantly at 37·5°, and distils at 297°–298° (corr.).

The *β cyanide* likewise passes over in the first instance at about 300°, as a liquid, but solidifies very quickly at ordinary temperatures. When purified by repeated crystallisation from ligroïn and rectification, it forms a beautiful white mass resembling stearin and melting at 66·5° (*i.e.* 29° higher than the *α* compound) to of melting potash on catechin, scoparin, luteolin, horse-chestnut tannin, and the red body formed by heating this tannin in an atmosphere of carbon dioxide:

$$\underset{\text{Catechin.}}{C^{19}H^{18}O^{8}} + O^{2} = \underset{\text{Phloroglucin.}}{2C^{6}H^{6}O^{3}} + \underset{\text{Protocatechuic acid.}}{C^{7}H^{6}O^{4}}$$

$$\underset{\text{Scoparin.}}{C^{21}H^{22}O^{10}} + O^{5} = C^{6}H^{6}O^{3} + 2C^{7}H^{6}O^{4} + CO^{2} + 2H^{2}O$$

$$\underset{\text{Luteolin.}}{C^{20}H^{14}O^{8}} + 2H^{2}O + O^{2} = 2C^{6}H^{6}O^{3} + C^{7}H^{6}O^{4} + CO^{2}$$

$$\underset{\text{Tannin of Horse-chestnut.}}{C^{26}H^{24}O^{12}} + O^{2} = 2C^{6}H^{6}O^{3} + 2C^{7}H^{6}O^{4}$$

$$\underset{\text{Red body.}}{C^{26}H^{22}O^{11}} + H^{2}O + O^{2} = 2C^{6}H^{6}O^{3} + 2C^{7}H^{6}O^{4}.$$

(Malin, *Ann. Ch. Pharm.* cxxxiv. 118. Hlasiwetz, *ibid.* cxxxviii. 190. Rochleder, *Bull. Soc. Chim.* [2] viii. 115, 122). Ratanhia-red, tormentil-red, and the phlobaphene of the oak have the same composition as horse chestnut-red, and are decomposed by fusion with potash in the same manner (Grabowski, *Jahresb.* 1867, p. 483; *Zeitschr. f. Chem.* [2] iv. 508. Rembold, *ibid.* 571).—2. Together with protocatechuic acid, paraoxybenzoic acid, and other products, by fusing dragon's blood or gamboge with caustic potash (Hlasiwetz a. Barth, *Jahresb.* 1865, p. 575; 1866, pp. 628, 631).

Phloroglucin heated to 140° with saturated aqueous *hydriodic acid* is not reduced (even in presence of phosphorus), but is converted, by abstraction of water, according to the equation $2C^{6}H^{6}O^{3} - H^{2}O = C^{12}H^{10}O^{5}$, into a new body which crystallises in nearly tasteless scales, slightly soluble in warm water and alcohol, insoluble in ether, and consisting of $C^{12}H^{10}O^{5} + 2H^{2}O$. The water is given off at 120° (Hlasiwetz, *Zeitschr. f. Chem.* [2] i. 613).

A moderately dilute solution of phloroglucin mixed with a similar solution of *quinine sulphate* slightly acidulated with sulphuric acid, yields large concentrically grouped needles consisting of a compound of quinine sulphate and phloroglucin, $C^{20}H^{24}N^{2}O^{2}.SO^{4}H^{2}.C^{6}H^{6}O^{3} + 2H^{2}O$. Orcin and resorcin form similar compounds with quinine sulphate (Hlasiwetz, *loc. cit.*).

PHLOROL or **PHLORYL ALCOHOL**, $C^{8}H^{10}O = C^{6}H^{4}\left\{\begin{matrix}CH^{2}(CH^{3})\\OH\end{matrix}\right.$, is one of the constituents of beech-tar creosote, and is obtained by repeated fractional distillation of the portion boiling between 217° and 220°. When dehydrated by distillation over sodium, it forms a colourless oily liquid boiling at 219°–220°, and gradually turning reddish when exposed to light (Marasse, *Ann. Ch. Pharm.* clii. 75).

PHLORONE. $C^{8}H^{8}O^{2}$.—This body, homologous with quinone, was discovered by Rommier a. Bouilhon (iv. 496), who obtained it by oxidising coal-tar creosote with sulphuric acid and manganese dioxide. Gorup-Besanez a. von Rad (*Zeitschr. f. Chem.* [2] iv. 560) have obtained it in like manner from that kind of Rhenish beech-tar creosote which consists mainly of cresol. The liquid mixed with 1½ times its weight of strong sulphuric acid, is left to stand for 24 hours, then diluted with 6 vol. water, and distilled at a gentle heat with 1½ times its weight of manganese dioxide. A yellow liquid then passes over, which soon deposits phlorone in yellow crystals and solidifying oily drops, while the condensing tube becomes filled with long yellow needles. The crystals are collected, the yellow distillate is agitated with ether, the ethereal solution evaporated, and the crystals thus obtained, together with those first deposited, are recrystallised from alcohol. In preparing phlorone from coal-tar creosote, it is also necessary to leave the mixture of the creosote with sulphuric acid to stand till it no longer becomes turbid on addition of water; otherwise it yields by oxidation a brown liquid, but no phlorone. Cresol boiling at 198° yields abundance of phlorone when oxidised as above; but xylylic phenol boiling at 214° yields only a brown unctuous mass, with very little phlorone. Guaiacol prepared by dry distillation of guaiac resin yields a body very much like phlorone, but possibly consisting of its next lower homologue (v. Rad, *Ann. Ch. Pharm.* cli. 158; *Zeitschr. f. Chem.* [2] v. 712).

Phlorone crystallises in golden-yellow oblique rhombic prisms, which when heated give off a pungent odour, attacking the eyes and mucous membranes; it sublimes without decomposition at a stronger heat, and volatilises even at ordinary temperatures. It is heavier than water, melts at a temperature above 100° (v. Rad; at 61°–62° according to Rommier a. Bouilhon), dissolves sparingly in cold, easily in boiling water, also in alcohol and ether. Its solutions colour the skin deep brown. Sulphuric acid dissolves it with yellow colour; alkalis impart to its solutions a brown colour, which disappears on addition of sulphuric acid. Dilute nitric acid dissolves it with yellow colour; with strong hydrochloric acid at the boiling heat it forms a brown solution which on cooling deposits white crystals of chlorhydrophlorone. With solid potash it forms a green mass. Phlorone solutions are decolorised by sulphurous acid and stannous chloride; ferric chloride colours them brown; hydrogen sulphide produces a precipitate.

Chlorophlorones (v. Rad, *loc. cit.*).—When dry chlorine is passed over moderately heated phlorone as long as hydrochloric acid continues to be evolved, the phlorone deliquesces to a yellow liquid, which on cooling deposits crystals, separable by means of alcohol into monochlorophlorone and dichlorophlorone, the former being the more soluble of the two. The same products are obtained by treating phlorone with hydrochloric acid and potassium chlorate.

Monochlorophlorone, $C^8H^7ClO^2$, crystallises in yellow needles melting below 100° to a brown liquid which resolidifies in the crystalline form on cooling. It has a peculiar aromatic odour, and dissolves easily in alcohol, ether, and acetic acid. Its solution in weak alcohol, boiled and left to cool, deposits a brown crystalline body, perhaps brown chlorhydrophlorone. When sulphurous acid gas is passed into warm water in which monochlorophlorone is suspended, the liquid on cooling deposits colourless crystals of monochlorohydrophlorone. Strong sulphuric acid dissolves monochlorophlorone, forming a deep yellow solution; potassium nitrite heated with it produces a fine red-brown colour. Its solution in acetic acid is coloured by soda-ley first green, then brown; the alcoholic solution is immediately coloured brown by soda or ammonia.

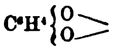
Dichlorophlorone, $C^8H^6Cl^2O^2$, forms light yellow unctuous laminæ very slightly soluble in cold alcohol, easily in hot alcohol, boiling acetic acid, and ether; it dissolves with yellow colour in strong sulphuric acid, and is turned brown in alcoholic solution by soda, ammonia, and ferric chloride.

Hydrophlorone, $C^8H^{10}O^2$, is produced by passing sulphurous acid gas into a saturated aqueous solution of phlorone containing phlorone in suspension, till all the crystals have become colourless. It crystallises from hot water in colourless nacreous laminæ, melts and sublimes when heated, dissolves easily in water, especially when heated, also in alcohol and ether. Ammonia colours the solutions brown, changed to dark red by heating or by contact with the air. With soda-ley a green colour is produced, becoming brown in contact with the air. By boiling with ferric chloride, dilute nitric acid, or silver nitrate, hydrophlorone is oxidised to phlorone, in the latter case with precipitation of metallic silver. Boiled with solution of cupric acetate it throws down cuprous oxide, and emits a strong odour of phlorone. With solid potash it forms a dark green mass. Fuming sulphuric acid dissolves it, with red colour, and the solution, diluted with water and neutralised with barium carbonate, contains a barium salt very soluble in water, insoluble in absolute alcohol. The aqueous solution of this acid colours ferric chloride dark brown, reduces silver salts, and forms a white precipitate with lead acetate.

Chlorhydrophlorone, $C^8H^9ClO^2$, is prepared by boiling phlorone crystals with strong hydrochloric acid. After repeated crystallisation from hot water it forms colourless silky needles, melting when heated to a brown liquid which solidifies to a colourless crystalline mass, and subliming with partial decomposition in colourless shining laminæ mixed with violet needles; it dissolves easily in hot water, alcohol, and ether. Solid chlorhydrophlorone is coloured violet by ferric chloride and forms a green mass with potash. Its solutions are coloured brown by ammonia and fixed alkalis, reduce silver nitrate when heated, giving off the odour of chlorophlorone, and precipitate cuprous oxide when heated with cupric nitrate (v. Rad).

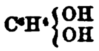
Dichlorhydrophlorone, $C^8H^8Cl^2O^2$, is produced by passing sulphurous acid gas into water in which dichlorophlorone is suspended, and warming the liquid on the water-bath till the yellow laminæ become colourless; it is purified by washing with cold water, crystallisation from boiling water, and finally from moderately heated acetic acid. It sublimes with partial decomposition, yielding dark brown needles which burn with green-edged flame when heated on platinum foil. It dissolves sparingly in cold, easily in hot water, very easily in ether, alcohol, and strong acetic acid. In potash-ley it dissolves with green colour, changing to brown-red; in warm sulphuric acid with deep brown colour. The alcoholic solution is coloured brown by ammonia, and then yields with hydrochloric acid a violet flocculent precipitate. It reduces silver nitrate and cupric acetate, and is converted by hydrochloric acid and potassium chlorate into yellow crystalline laminæ. With ferric chloride it immediately yields a violet flocculent precipitate, perhaps analogous to violet dichlorhydroquinone.

Phlorone may be formulated either as ethyl-quinone, $C^6H^3(C^2H^5)O^2$, or as dimethylquinone; but, since the highest chlorinated product obtainable from it by the action of chlorine or of hypochlorous acid, is dichlorophlorone, it appears to have only two atoms of hydrogen easily replaceable by chlorine, and is therefore most probably dimethylquinone; in like manner dichlorhydrophlorone may be regarded as dimethylhydroquinone:



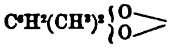
$C^6H^4\left\{\begin{matrix}O\\O\end{matrix}\right.$

Quinone.



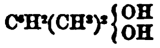
$C^6H^4\left\{\begin{matrix}OH\\OH\end{matrix}\right.$

Hydroquinone.



$C^6H^2(CH^3)^2\left\{\begin{matrix}O\\O\end{matrix}\right.$

Phlorone.



$C^6H^2(CH^3)^2\left\{\begin{matrix}OH\\OH\end{matrix}\right.$

Hydrophlorone.

PHLORYL ALCOHOL. Syn. with PHLOROL (p. 927).

PHOSENE. See PHOTENE.

PHOSGENE. Syn. with CARBON OXYCHLORIDE (p. 405).

PHOSPHAMIC ACIDS. Gladstone has described three phosphamic acids derived from pyrophosphoric acid by substitution of 1, 2, and 3 at. amidogen for hydroxyl (iv. 766); these may be formulated as follows:

Pyrophosphoric acid	$\left.\begin{matrix}P(HO)^2O\\P(HO)^2O\end{matrix}\right\}O.$
Pyrophosphamic acid	$\left.\begin{matrix}P(NH)^2(HO)O\\P(HO)^2O\end{matrix}\right\}O.$
Pyrophosphodiamic acid	$\left.\begin{matrix}P(NH^2)(HO)O\\P(NH^2)(HO)O\end{matrix}\right\}O.$
Pyrophosphotriamic acid	$\left.\begin{matrix}P(NH^2)^2O\\P(NH^2)(HO)O\end{matrix}\right\}O.$

The following are additional details respecting these acids (*Chem. Soc. J.* [2] vi. 64):

Pyrophosphamic acid, $P^2(NH^2)H^3O^6$, is produced by the decomposition of the tetraphosphamic acids (p. 931); also by the following methods: *a.* When pyrophosphoric acid is saturated with ammonia, and barium hydrate is added not in excess, a white precipitate of barium pyrophosphamate is obtained; with excess of baryta, pyrophosphate is the only product. A similar result is produced when lead acetate or ferric chloride is added instead of barium hydrate.—*β.* A salt having the composition of ferric pyrophosphamate is likewise formed when insoluble ferric pyrophosphate is precipitated in presence of a large quantity of sal-ammoniac; or by dissolving ferric pyrophosphate in ammonia and precipitating with sulphuric acid; or again by precipitating soluble ferric pyrophosphate from its solution in sulphuric acid by ammonia. The compound thus obtained differs however from the ferric pyrophosphamate previously described, in being soluble in sodium pyrophosphate and in ferric chloride, slightly also in water, and in being decomposed by cold dilute sulphuric acid. It may therefore be regarded either as a soluble modification of ferric pyrophosphamate, $[P^2(NH^2)O^6]^2Fe^2 + 2H^2O$, or perhaps only as ammonio-ferric pyrophosphate, $(P^2O^7)^2(NH^4)^2Fe^2$. It is not converted into the ordinary salt by boiling with very dilute sulphuric acid. Copper salts give similar results.

Pyrophosphodiamic acid, $P^2(NH^2)^2H^2O^5$, is most distinctly characterised by the white flocculent precipitate thrown down from its hot strongly acid solution by ferric chloride; this precipitate does not melt when heated, but blackens, gives off ammonia, and forms a sublimate, whereas ferric pyrophosphate merely melts without blackening.

Pyrophosphotriamic acid, $P^2(NH^2)^3HO^4$, is most abundantly produced by saturating phosphorus oxychloride (not cooled) with ammonia gas, heating the product to 220°, and boiling it for a short time with water.

With regard to the formation of these amidated acids from phosphorus oxychloride, Gladstone supposes that the oxychloride reacts in the cold with 2 mol. ammonia, so as to form the amide $P(NH^2)Cl^2O$, and at higher temperatures with 4 mol. ammonia to form the amide $P(NH^2)^2ClO$. The formation of pyrophosphodiamic acid from these amides takes place in the manner shown by the following equations:

$$2P(NH^2)Cl^2O + 3H^2O = 4HCl + P^2(NH^2)^2H^2O^5.$$
$$2P(NH^2)^2ClO + 3H^2O = 2NH^4Cl + P^2(NH^2)^2H^2O^5.$$

Pyrophosphamates are formed by the action of metallic chlorides on the diamic acid, thus:

$$P^2(NH^2)^2H^3O^5 + H^2O + 3MCl = NH^4Cl + 2HCl + P^2(NH^2)M^3O^6.$$

Pyrophosphotriamic acid appears to be formed from an amidated oxychloride of unknown composition.

TETRAPHOSPHAMIC ACIDS (Gladstone, *Chem. Soc. J.* [2] vi. 261).—These acids, also produced by the action of water on the amides of phosphorus oxychloride, may be derived from tetraphosphoric acid, $P^4(HO)^6O^7$, the acid corresponding to the phosphates, $P^4(MO)^6O^7$ (iv. 537); thus:

Tetraphosphodiamic acid	$P^4(NH^2)^2(HO)^4O^7$.
Tetraphosphotetramic acid	$P^4(NH^2)^4(HO)^2O^7$.

When phosphorus oxychloride is saturated at a low or moderately high temperatures with ammonia, a white mass is formed which dissolves completely in water, with exception of a small quantity of pyrophosphotriamic acid; and alcohol added to this solution throws down either a viscid liquid or light solid precipitate, sometimes also a glutinous substance which appears to be a mixture of the other two. The liquid compound, when purified by washing with alcohol, repeated precipitation by alcohol from its aqueous solution, and drying in a vacuum, has the composition $P^4N^5H^{17}O^{11}$. It is very hygroscopic, sustains a temperature of 100° without decomposition, gives off ammonia when treated with cold potash-ley, and is decomposed by hydrochloric acid into orthophosphoric acid and sal-ammoniac. With ammonia it forms a liquid compound slightly soluble in water, insoluble in alcohol, from which the original substance is separated by dilute sulphuric acid. In aqueous solution it forms solid precipitates with many metallic salts, but appears at the same time to undergo alteration, inasmuch as neither of these compounds contains more than 3 at. nitrogen to 4 at. phosphorus, and they all, when decomposed by acids, yield solid tetramides and pyrophosphamic acids. From its reaction with potash, the compound $P^4N^5H^{17}O^{11}$ may be regarded as the triammonium salt of *tetraphosphodiamic acid*, $P^4(NH^2)^2H(NH^4)^3O^{11}$.

Tetraphosphotetramic acid, $P^4(NH^2)^4H^2O^9$, is obtained either by decomposing the liquid compound with a metallic salt, and the precipitate with an acid, or more readily by dissolving the above-mentioned glutinous body in water, decomposing it with a large excess of a mineral acid, precipitating with alcohol, and repeating this treatment till the precipitate becomes sparingly soluble in water, and friable after drying. It is likewise produced by boiling the liquid acid with water for several hours, or by treating it with alkalis or strong acids. Its formation is usually accompanied by that of pyrophosphodiamic or pyrophosphotriamic acid. It combines with bases, and is separated by acids from the resulting compounds, apparently unaltered. It appears to form two ammonium salts, one of which, precipitated by alcohol from the aqueous solution, has the composition $P^4(NH^2)^4H(NH^4)O^9$, and gives off all its ammonia in a vacuum. Two *silver salts*, $P^4N^4H^4Ag^4O^9$ and $P^4N^4H^8Ag^2O^9$, have also been examined.

Tetraphosphopentazotic Acid. $P^4N^5H^9O^7$.—When phosphorus oxychloride is rapidly saturated with ammonia, the mass becomes strongly heated, and when treated with water leaves a body different from pyrophosphotriamic acid. This compound is obtained in greater purity when the product, saturated with ammonia, is heated above 200°, but not to the volatilising point of sal-ammoniac, and then exhausted with water. The insoluble residue consists of tetraphosphopentazotic acid. It is decomposed with moderate facility by water, and quickly at the boiling heat, with formation of pyrophosphamic acids; a similar transformation takes place gradually in the dry state and at ordinary temperatures. The salts of this acid are nearly or quite insoluble. The ammonium salt, $P^4N^5H^8(NH^4)O^7$, and the potassium salt, $P^4N^5H^8KO^7$, have been examined; also the silver, copper, and lead salts, which, however, have not been obtained of constant composition.

When tetraphosphopentazotic acid is treated with neutral or slightly acidulated silver nitrate, a pale yellowish-brown precipitate is formed, having nearly the composition $P^4N^4H^4Ag^2O^7$. Gladstone regards this salt as the silver salt of *tetraphosphotetrimic acid*, $P^4(NH)^4H^2O^7$ (*Chem. Soc. J.* [2] vii. 22).

PHOSPHAMIDES. By passing dry ammonia gas into phosphorus oxychloride, and digesting the product with water to dissolve sal-ammoniac, Schiff (iv. 498) obtained phosphotriamide, $PO(NH^2)^3$. Gladstone, on the other hand, did not obtain this compound, but only the intermediate bodies $POCl^2(NH^2)$ and $POCl(NH^2)^2$ (*Chem. Soc. J.* [2] vii. 16). Schiff, however, in a recent paper (*Zeitschr. f. Chem.* [2] v. 609) again asserts the formation of the phosphotriamide, and points out that in order to ensure the complete replacement of the chlorine in $POCl^3$ by amidogen, it is necessary to use *perfectly dry* ammonia gas, to pulverise the mass frequently during the operation, again treat it with ammonia, while warmed, and finally leave it for some time in the pulverised state in a vessel filled with ammonia gas, agitating it frequently to promote the absorption. If phosphoric acid be represented as $P\left\{\begin{matrix}O.OH\\OH\\OH\end{matrix}\right.$ and phosphorus oxychloride accordingly as $P\left\{\begin{matrix}O.Cl\\Cl\\Cl\end{matrix}\right.$, it will be seen that one atom of chlorine in the latter may have a different function from the rest, and may be more difficult to replace by amidogen. If the oxychloride used retains a small quantity of pentachloride, the phosphotriamide formed as above will contain a certain quantity of chlorine, inasmuch as the pentachloride is decomposed by ammonia according to one of the following equations:

$$PCl^5 + 4NH^3 = \underset{\substack{\text{Nitrogen}\\\text{Phosphochloride.}}}{NPCl^2} + 3NH^4Cl$$

or

$$PCl^5 + 5NH^3 = \underset{\substack{\text{Chloropho-}\\\text{phamide.}}}{N^2\left\{\begin{matrix}PCl^2\\H^3\end{matrix}\right.} + 3NH^4Cl.$$

In the latter case, on dissolving out the sal-ammoniac by water, **phosphodiamide** would be formed:

$$N^2\left\{\begin{matrix}PCl^2\\H^3\end{matrix}\right. + H^2O = 2HCl + N^2\left\{\begin{matrix}PO\\H^3\end{matrix}\right..$$

Phospho-phenyldiamide or *Phospho-dianilide*, $N^2(PO)'''(C^6H^5)^2$, is formed in like manner by the action of phosphorus pentachloride on aniline, and remains, on treating the product with water, as a white flocculent substance. Heated with water it melts somewhat below 100° and is gradually converted into aniline phosphate. With phosphorus trichloride, aniline forms the *trianilide of phosphorous acid*, together with aniline hydrochloride:

$$PCl^3 + 6C^6H^7N = 3(C^6H^7N.HCl) + P(NH.C^6H^5)^3.$$

The trianilide which is the less soluble part of the crude product is gradually converted by the action of water into aniline phosphite (Schiff).

Phenyl-sulphuryl-dichlorophosphamide, $C^6H^5.SO^2.NH.PCl^2$, is formed by the action of phosphorus pentachloride on the so-called benzene-sulphamide:

$$C^6H^5.SO^2NH^2 + PCl^5 = Cl^2 + HCl + C^6H^5.SO^2.NH.PCl^2.$$

The crude product poured while still warm on a porous plate, and then left for some time over sulphuric acid, solidifies at first, but afterwards becomes semifluid, an oily liquid sinking into the plate. The remaining solid compound crystallises from ether in large shining crystals, which must be enclosed immediately in a sealed tube to preserve them from alteration. They melt at 130°–131°, and are reconverted into benzene-sulphamide by contact with moist air, or more quickly by water or alcohol (Wichelhaus, *Zeitschr. f. Chem.* [2] vi. 54).

PHOSPHANILINE. $(C^{18}H^{18}P''')N^3$ (Tait, *Zeitschr. f. Chem.* [2] i. 648).—When well-cooled aniline is mixed by drops with phosphorus trichloride, violent reaction takes place, and an unctuous mass is formed, the aqueous solution of which, freed from excess of aniline by passing through a wet filter, solidifies by evaporation in a vacuum over sulphuric acid to a mass of needle-shaped crystals, consisting of the hydrochloride of phosphaniline formed by direct combination of aniline and phosphorus trichloride:

$$3C^6H^7N + PCl^3 = C^{18}H^{18}PN^3.3HCl.$$

The *platinochloride*, $2(C^{18}H^{18}PN^3.3HCl).3PtCl^4$, forms pale yellow granular crystals soluble in water and alcohol, but not in ether. A *zincochloride*, $2(C^{18}H^{18}PN^3.3HCl).3ZnCl^2$, is obtained in somewhat deliquescent needles soluble in alcohol, by dissolving zinc in the acidulated solution of the hydrochloride, and evaporating at about 93°. The hydrochloride also forms double salts with cadmic, cupric, and mercuric chlorides. Bromine-water produces in the solution of the hydrochloride a brown precipitate containing tribromaniline. Phosphaniline itself has not been isolated.

PHOSPHIDE, CYANETHYLIC. $P\left\{\begin{matrix}CN\\ C^2H^5\\ H\end{matrix}\right.$.—Produced by the action of gaseous hydrogen phosphide on cyanogen chloride dissolved in ether. The reaction takes place easily at 100°, and on distilling off the ether, the cyanethylic phosphide remains as a liquid, which solidifies in a dry atmosphere. It crystallises in rhombic plates, melts at 49°–50°, volatilises without decomposition, and dissolves easily in water, alcohol, and ether. Its formation is represented by the equation:

$$CNCl + PH^3 + (C^2H^5)^2O = HCl + C^2H^6O + P(CN.H.C^2H^5).$$

When oxidised it gives off an odour of aldehyde or acetic acid (Darmstädter a. Henniger, *Compt. rend.* lxx. 404).

PHOSPHONITRILE. This name is now applied by Gladstone to the compound PNO (Gerhardt's biphosphamide), which may also be regarded as phosphomonamide, $N(PO)'''$. It is produced by strongly heating the product obtained by the action of ammonia on phosphorus oxychloride, being formed by abstraction of 2HCl from the compound $PCl^2(NH^2)O$, or of NH^4Cl from $PCl(NH^2)^2O$ (Gladstone, *Chem. Soc. J.* [2] vii. 18).

PHOSPHONITRYLIC ACID. P^2NHO^4.—From observations by Holmes, reported by Gladstone (*ibid.* 79), it appears that the potassium salt of this acid is obtained by igniting potassium pyrophosphotriamate:

$$P^2N^3H^6KO^5 = 2NH^3 + P^2NKO^4.$$

The *ammonium salt* appears to be formed by ignition of pyrophosphotetramic acid:

$$P^2N^3H^7O^4 - NH^3 = P^2N(NH^4)O^4.$$

PHOSPHORUS. On the atomicity of phosphorus, see Wichelhaus (*Ann. Ch. Pharm. Suppl.* vi. 257; *Jahresb.* 1868, p. 148).

Modifications.—Hittorff (*Pogg. Ann.* cxxvi. 193; *Jahresb.* 1865, p. 127) has obtained a crystallised modification of red phosphorus, by heating amorphous phosphorus to 530° in a sealed vacuous glass tube, and allowing the vapour to condense in the upper part of the tube, heated only to 447°; the phosphorus then collects in nodular groups of microscopic needles. It may however be obtained in larger quantity and more distinct crystals, by separation from a solution of phosphorus in lead. A wide tube of difficultly fusible glass is filled to one-fourth with phosphorus, and the remaining three-fourths with lead, while a stream of carbon dioxide is passed through it. It is then exhausted, sealed, enclosed in an iron tube packed with magnesia, and heated for several hours over a number of Bunsen burners. On cooling, the surface of the lead is found to be covered with black, metallically lustrous, laminar crystals, unalterable in the air, while the interior of the lead is traversed by small but dense and well-defined crystals. The superficial crystals are very thin, mostly bent and transversely striated, whereby they acquire the aspect of rows of prismatic crystals; they are yellowish-red by transmitted light. The crystals enclosed in the mass of lead are isolated by treating this mass for several days with nitric acid of sp. gr. 1·1 (the phosphorus, as the more electro-negative body, not being attacked), and purified from all but a trace of lead by boiling with strong hydrochloric acid. They have then a black-violet colour, and appear under the microscope as rhombohedrons nearly approaching to the cube, and probably isomorphous with arsenic, antimony, and bismuth. The sp. gr. of the laminar and also of the dense crystals (allowance being made for the small quantity of lead which they retain) is 2·34 at 15°: hence the specific volume of crystallised red phosphorus is 13·25, agreeing with that of crystallised arsenic, according to the specific gravity 5·67 determined by Hittorf. The crystallised red phosphorus is even less volatile than amorphous phosphorus, and like the latter conducts electricity feebly in comparison with metals, but easily as compared with ordinary phosphorus. Hittorf designates this variety of phosphorus as *crystallised metallic*, red amorphous phosphorus as *amorphous metallic*, and ordinary colourless phosphorus as *ordinary non-metallic*.

Ordinary phosphorus is most easily converted into amorphous phosphorus by heating it to the temperature of boiling sulphur in a thick glass tube (or an iron vessel for larger quantities) exhausted and sealed. The transformation is attended with evolution of heat, the temperature of the phosphorus vapour exceeding that of the heated air-bath by about 75°. The conversion of ordinary into amorphous phosphorus in presence of iodine takes place at 160°. Respecting the vapour-densities and vapour-tensions of the three varieties, see the memoir above cited; also *Phil. Mag.* [4] xxxi. 311; *Chem. News*, xiii. 133; *Jahresb.* 1865, p. 130. On the conversion of ordinary into amorphous phosphorus, and the contrary, see Lemoine (*Bull. Soc. Chim.* [2] viii. 71; *Jahresb.* 1867, p. 138).

From experiments on the formation of white phosphorus (iv. 503), Baudrimont (*Bull. Soc. Chim.* [2] v. 206) concludes that this modification is neither crystallised nor allotropically modified phosphorus, but ordinary phosphorus having its surface corroded by oxygen dissolved in the water in which it is kept; in de-aërated water the white film is not produced. The presence of water appears however to be necessary, inasmuch as phosphorus does not lose its transparency when it oxidises in the air.

Fusion of Phosphorus.—Phosphorus fused under water does not solidify at temperatures above 32° C., either by the most violent agitation in a closed tube, or in an open tube by contact with any solid body, even with amorphous phosphorus heated to the same temperature; immediately however if brought in contact with ordinary phosphorus (a glass tube on which phosphorus has been rubbed), or if a solid body immersed in the fused mass is rubbed against the sides of the tube or against another immersed body. Particles of glass, for example, heated with the phosphorus do not prevent it from remaining fluid as it cools, but on shaking the tube they instantly induce solidification, even at 43°, the temperature then rising to 44° (Gernez, *Compt. rend.* lxiii. 217).

Sublimation.—According to Blondlot (*ibid.* 397), colourless phosphorus may be sublimed in a rarefied atmosphere of nitrogen at comparatively low temperatures, e.g. by melting phosphorus in a small flask previously sealed, and, after the oxygen of the confined air has been absorbed, immersing the lower part of the flask in an air-bath heated to 40°; the phosphorus then sublimes in the neck in colourless microscopic cubic crystals having an adamantine lustre.

Oxidation.—Groves (*Pharm. J. Trans.* [2] vi. 643) found that amorphous phosphorus which had been kept for two years in a cracked vessel, was converted, to the extent of about 16 p. c. into phosphorous and phosphoric acids. The damp mass emitted the odour of oxidising phosphorus, but was not luminous in the dark.

According to Blondlot (*Zeitschr. f. Chem.* [2] iv. 375), the direct product of the slow oxidation of phosphorus is not phosphorous, but phosphoric acid; and the phosphorous acid contained in the so-called *phosphatic acid* (iv. 499) is produced by the action of the free phosphorus on phosphoric acid previously formed. White phosphorus fumes consist wholly of phosphoric acid. The formation of ozone in the oxidation of phosphorus does not take place at temperatures below 12°. Respecting the composition of phosphorus fumes, see also W. Schmid (*J. pr. Chem.* xcviii. 414; *Jahresb.* 1866, p. 113).

Phosphorus as a Test for Metals.—A solution of phosphorus in carbon bisulphide filtered through asbestos, and then shaken up with water, whereby a snow-white turbidity is produced, affords a very delicate test for certain metals. All copper solutions, even ammoniacal, give with this reagent a brown-red precipitate, silver solutions a black, mercuric solutions a brownish-yellow, gold-solutions a [illegible] precipitate. Still greater delicacy may be obtained by the use of filtering-paper moistened with the liquid above mentioned, and not quite dried (W. Schmid, *Zeitschr. f. Chem.* [2] iv. 161). On the reactions of phosphorus with metals, see also Nicklès (*ibid.* v. 351).

Detection and Estimation of Phosphorus.—The presence of phosphorus either in inorganic or in organic bodies may be detected by heating the solid substance (or the charcoal in the case of organic bodies) with about half its bulk of magnesium filings in a test-tube. The mixture becomes phosphorescent in the dark, and red phosphorus is deposited on the sides of the tube, the greater part of the phosphorus however, uniting with the magnesium. On moistening the contents of the tube after cooling, with water, gaseous hydrogen phosphide is given off (Schönn, *Zeitschr. anal. Chem.* 1869, pp. 53, 55; *Zeitschr. f. Chem.* [2] v. 664).

In applying the process given by Dusart and by Blondlot (iv. 520) for the detection of phosphorus, Otto (*Zeitschr. f. Chem.* [2] ii. 733) recommends that the gas be passed through a U-tube containing pumice soaked in potash-ley, in order to remove hydrogen sulphide or sulphurous oxide; without this precaution, the emerald-green colouring of the flame, even when a rather large quantity of phosphorus is present, partly disappears, and is disguised by a blue flame, arising, as shown by Barrett (*Phil. Mag.* [4] xxx. 321), from the presence of sulphur-compounds.

For the estimation of phosphorus in iron and steel, Spiller (*Chem. Soc. J.* [2] iv. 148) mixes the nearly neutralised solution of the metal in nitro-muriatic acid—after partial reduction with sulphurous acid and cooling to 20°–24°—with sesquicarbonate of ammonia, till the precipitate, which is red at first, assumes a greenish colour. The precipitate containing all the phosphoric acid is then dissolved in hydrochloric acid; the iron is precipitated by ammonium sulphide after addition of citric acid and ammonia; and in the filtrate freed from sulphur the phosphoric acid is precipitated as ammonio-magnesian phosphate.

Schlœsing (*Zeitschr. f. Chem.* [2] iv. 567; *Jahresb.* 1868, p. 856) estimates phosphorus in iron phosphide by igniting the pulverised compound in chlorine gas, passing the evolved phosphorus trichloride into water, and oxidising the resulting phosphorous acid to phosphoric acid by nitric acid. Tantin (*Chem. News*, xviii. 252) estimates phosphorus in iron by dissolving the iron in dilute hydrochloric acid, passing the evolved gas through potash-ley to remove hydrogen sulphide, and then into a solution of silver nitrate, which absorbs the hydrogen phosphide (and arsenide, if arsenic is present). The precipitated silver phosphide is treated with nitromuriatic acid, and the phosphoric acid thereby formed is precipitated as ammonio-magnesian phosphate,

Chlorine- and Bromine-compounds of Phosphorus.

According to Rathke (*Zeitschr. f. Chem.* [2] vi. 57), the statement of Carius that phosphorus pentachloride and carbon bisulphide yield, by their mutual action, sulphocarbonyl chloride, $\mathrm{CSCl^2}$, is incorrect. The products actually obtained are carbon tetrachloride and phosphorus sulphochloride, according to the equation: $\mathrm{CS^2 + 2PCl^5 = CCl^4 + 2PSCl^3}$.

Phosphorus trichloride treated with 1 mol. absolute alcohol gives off a large quantity of hydrochloric acid, and the liquid product yields, by distillation between 90° and 125°, ***ethyl-phosphorous chloride***, $\mathrm{POC^2H^5Cl^2}$, which by fractional distillation is obtained as a transparent, colourless, strongly refracting liquid, fuming in the air, boiling constantly at 170°, and having a sp. gr. of 1·316 at 0°. Its formation is represented by the equation:

$$\mathrm{PCl^3 + C^2H^6O = HCl + POC^2H^5Cl^2}.$$

It is decomposed by water into alcohol and phosphorous acid. By bromine it is resolved, according to the equation,

$$\mathrm{POC^2H^5Cl^2 + Br^2 = C^2H^5Br + POCl^2Br},$$

into ethyl bromide and phosphorus oxychlorobromide, which may be separated by fractional distillation (Menschutkin, *Ann. Ch. Pharm.* cxxxix. 343).

Butyl-phosphorous chloride, $\mathrm{POC^4H^9Cl^2}$, produced by the action of 2 mol. $\mathrm{PCl^3}$ on 3 mol. butyl alcohol, boils between 154° and 156°, has a sp. gr. of 1·191 at 0°, and is decomposed by water in the same manner as the ethyl-compound. ***Amyl-phosphorous chloride***, $\mathrm{POC^5H^{11}Cl^2}$, obtained like the preceding, boils at 173°, has a sp. gr. of 1·109 at 0°, and reacts like the ethyl-compound with water and bromine (Menschutkin).

Phosphorus Oxychlorobromide, $\mathrm{POCl^2Br}$, obtained as above, is a transparent, colourless, strongly refracting liquid, quickly turning yellow. It boils at 135° to 137°, has a sp. gr. of 2·059 at 0°, and is decomposed by water with formation of phosphoric acid (Menschutkin).

The ***oxychlorochloride***, $\mathrm{POCl^2Cl}$, produced in like manner by the action of chlorine on ethylphosphorous chloride, agrees in sp. gr. (1·66), boiling point (110°), and other properties, with phosphorus oxychloride obtained by the ordinary methods. The oxychloride, and phosphoric acid which is formed from it by the action of water, may therefore be represented by the following formulæ:

$$\overset{'''}{\mathrm{P}}\left\{\begin{array}{l}\mathrm{OCl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{array}\right. \qquad\qquad \overset{'''}{\mathrm{P}}\left\{\begin{array}{l}\mathrm{O.OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{array}\right.$$

Oxychloride. Phosphoric acid.

Phosphoric acid thus appears to have the constitution of monoxyphosphorous acid (Wichelhaus, *Zeitschr. f. Chem.* [2] iii. 321).

Sulphochloride. $\mathrm{PSCl^3}$.—Chevrier (*Compt. rend.* lxiii. 1003) prepares this compound by gradually adding 2 at. phosphorus to 3 mol. sulphur chloride heated nearly to boiling in a capacious flask, and distilling after the whole is dissolved, rejecting the portion which passes over below 125°:

$$\mathrm{P^2 + 3S^2Cl^2 = S^4 + 2PSCl^3}.$$

By this method, 800 grms. of the sulphochloride may be prepared in the course of a day. According to A. v. Flemming (*Zeitschr. f. Chem.* [2] iv. 288), the product obtained by Chevrier's method is not pure, but may be purified, with loss of a considerable portion, by agitating it with water, separating it as well as possible from the watery liquid, distilling, and rejecting the portion which first passes over at 110°. Chevrier (*ibid.* v. 442) has given several details respecting the properties and reactions of this body, but they are not of much importance.

According to L. Henry (*Deut. chem. Ges. Ber.* ii. 638), the sulphochloride is formed by direct combination of sulphur and the trichloride at 130°. It boils at 125°-128° (compare iv. 606).

Hydrides. According to Rüdorff (*Zeitschr. f. Chem.* [2] ii. 637), the yellow body formed by the action of water on phosphorus di-iodide, commonly regarded as amorphous phosphorus, agrees in its properties with solid phosphorus hydride, P^2H or P^4H^2. On adding phosphorus iodide to hot water, this compound is immediately separated, and non-spontaneously inflammable phosphorus tri-hydride is given off. in cold water the reaction takes place gradually. Rüdorff represents it by the following equation:

$$40PI^2 + 48H^2O = 2P^4H^2 + 4PH^3 + 3P^2O^5 + 11P^2O^3 + 80HI.$$

According to Commaille (*J. Pharm.* [4] viii. 321), the tri-hydride is rapidly evolved by the action of phosphorus on potash-ley even at ordinary temperatures: hence an error may arise in the analysis of gases, when, after treatment of the gas with potash, phosphorus is introduced to absorb oxygen, and comes in contact with the potash.

Oxides and Oxygen-acids of Phosphorus.

Phosphorous Acid. PH^3O^3.—This acid is produced by atmospheric oxidation of hypophosphorous acid. A solution of barium hypophosphite decomposed by sulphuric acid, and exposed for a long time to the air, yielded, when neutralised with calcium carbonate, a precipitate of calcium phosphite (Rammelsberg, *Zeitschr. f. Chem.* [2] iv. 724).

When 1 mol. crystallised phosphorous acid and 1 mol. *bromine* are heated in a sealed tube to 100°, with frequent agitation, hydrobromic and metaphosphoric acids are produced:

$$PH^3O^3 + Br^2 = 2HBr + PHO^3.$$

With 3 mol. bromine to 4 mol. phosphorous acid, the products are orthophosphoric acid, hydrobromic acid, and phosphorus tribromide:

$$4PH^3O^3 + 3Br^2 = 3PH^3O^4 + 3HBr + PBr^3.$$

The action of *iodine* is not exactly analogous to that of bromine. With a small proportion of iodine, phosphorus iodide and metaphosphoric acid are found among the products. With a larger proportion of iodine, the products are orthophosphoric acid, hydriodic acid, phosphonium iodide, and phosphorus di-iodide:

$$8PH^3O^3 + 5I = 6PH^3O^4 + 2HI + PH^4I + PI^2$$

(Gustavson, *Bull. Soc. Chim.* [2] viii. 29). According to Ordinaire (*Compt. rend.* lxiv. 363), 1 mol. phosphorous acid and 2 mol. bromine heated in a sealed tube, form, together with hydrobromic acid, a very deliquescent crystallised body, which he regards as monobromophosphorous acid; it is decomposed by boiling water, with formation of a new gelatinous acid. Dry chlorine at 100° acts in a similar manner. The formation of phosphoric acid was not observed in either case.

Metallic Phosphites.—The constitution of these salts has been carefully examined by Rammelsberg (*Berl. Akad. Ber.* 1866, p. 537; *Chem. Soc. J.* [2] v. 388; further *Pogg. Ann.* cxxxi. 263, 359; cxxxii. 481; *Jahresb.* 1867, p. 141). His experiments confirm the view advocated by H. Rose (*Pogg. Ann.* viii. 205; ix. 23, 215), that different phosphites contain different quantities of chemically combined or constitutional water, or its elements (exclusive of water of crystallisation), in opposition to that of Wurtz, according to which, all dry phosphites contain the same amount of constitutional water, namely 1 molecule. Rammelsberg does not however regard the existence of the salts $M''HPO^3$ (or $\overset{''}{M}{}^2H^2P^2O^6$) and $\overset{''}{M}{}^2H^4P^2O^7$ as demonstrating the existence of two different phosphorous acids, $H^6P^2O^6$ and $H^8P^2O^7$, or the evolution of hydrogen from heated phosphorous acid as a proof that the hydrogen does not exist therein in the form of water. He infers rather, from the whole of the facts observed, that both crystallised phosphorous acid and the metallic phosphites contain water ready formed, but more intimately combined than in other hydrates, so that it is not given off below 200°, and its elements take part in the decomposition of soluble in water. The *ammonium salt* separates on mixing a hot ammoniacal solution of the acid with concentrated solution of sal-ammoniac, as an orange-coloured precipitate which crystallises from boiling water in thin needles. The *calcium salt*, $[C^{10}H^{5}(NO^{2})^{2}O]^{2}Ca + 6H^{2}O$, forms long orange-yellow needles somewhat sparingly soluble in water, and becoming red, with loss of water, at 120°. The *silver salt*, $C^{10}H^{5}(NO^{2})OAg$, is a red flocculent precipitate, the solution of which in hot ammonia deposits crystals of the argent-ammonium salt. The *ethylic ether*, $C^{10}H^{5}(NO^{2})^{2}O.C^{2}H^{5}$, formed by heating the silver salt with ethyl iodide to 100°, crystallises from alcohol in long yellow needles melting at 88°, insoluble in water (Martius).

Dinitronaphthol is one of the most beautiful and permanent of yellow dyes, colouring silk and wool, without the aid of a mordant, in all shades from light lemon to deep gold-yellow. It is isomeric with the yellow naphthalene dye (perhaps β dinitronaphthol) which was patented in this country in 1863 in the name of W. Newton (*London Journal of Arts*, 1863, December, p. 348). This latter, prepared by boiling 100 pts. naphthalene with 200 pts. nitric acid of sp. gr. 1·30, and designated by Martius as *dinitronaphthylic acid*, is much more soluble in alcohol than α dinitronaphthol, and is converted by reduction with tin and hydrochloric acid into a brown resinous mass, whereas α dinitronaphthol similarly treated yields the basic compound *diamidonaphthol*, $C^{10}H^{6}(NH^{2})^{2}O$. The hydrochloric acid solution of this base supersaturated with potash, deposits, on exposure to the air, a yellow crystalline base, $C^{10}H^{8}N^{2}O$, which forms easily crystallisable, finely coloured, permanent salts, and is converted by boiling with water into an indifferent body, $C^{10}H^{7}NO^{2}$, crystallising in yellow-red needles:

$$C^{10}H^{8}N^{2}O + H^{2}O = C^{10}H^{7}NO^{2} + NH^{3}.$$

This latter is converted by boiling with hydrochloric acid (according to the equation $C^{10}H^{7}NO^{2} + H^{2}O = NH^{3} + C^{10}H^{6}O^{3}$) into a compound which crystallises in yellow needles or laminæ very slightly soluble in water, more soluble in alcohol, very soluble in ether, subliming when heated, and yielding by oxidation oxalic and phthalic acids (Martius a. Griess, *Ann. Ch. Pharm.* cxxxiv. 375).

Oxynaphthol. $C^{10}H^{8}O^{2} = C^{10}H^{6}(OH)^{2}$. *Naphthobioxyl.*—Produced by fusing disulphonaphthylene-sulphurous acid (v. 568), or its potassium salt, with potash:

$$C^{10}H^{6}(SO^{3}H)^{2} + 2KOH = C^{10}H^{6}(OH)^{2} + 2SO^{3}KH.$$

After precipitation from the potash solution by hydrochloric acid, and purification from a tarry substance by boiling with water, it crystallises in colourless needles or small rhombohedrons easily soluble in alcohol, ether, and chloroform, less easily in hot water. The solutions (not quite pure) exhibit a remarkable dichroïsm of blue and brown. Oxynaphthol dissolves easily in potash, the solution instantly turning black in contact with the air, and yielding with acids, after a while, a black precipitate. Heated in a test-tube to 230° it turns yellow and then brown, but does not fuse (Dusart, *Bull. Soc. Chim.* [2] viii. 200. Darmstädter a. Wichelhaus, *Deut. chem. Ges. Ber.* 1869, p. 113).

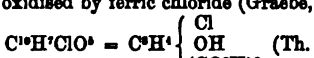
Dichloroxynaphthol, $C^{10}H^{6}Cl^{2}O^{2} = C^{6}H^{4}Cl^{2}(OH)^{2}$, is formed by the action of reducing agents on dichloronaphthoquinone (p. 853):

$$C^{10}H^{4}Cl^{2}O^{2} + H^{2} = C^{10}H^{4}Cl^{2}(OH)^{2}.$$

The reduction is most easily effected by heating in the water-bath with aqueous hydriodic acid and a small quantity of phosphorus, till the yellow crystals of dichloronaphthoquinone become colourless. By washing these crystals with water, dissolving them in alcohol, and evaporating or precipitating with water, dichloroxynaphthol is obtained in colourless crystals which quickly turn reddish on exposure to the air. It is quite insoluble in cold water, only slightly soluble in hot water, easily in alcohol and ether. It melts at 135°–140°, turns brown and decomposes partially at a higher temperature. Alkalis dissolves it readily, forming a solution which is colourless at first, but soon acquires the colour of the chloroxynaphthalates. Ferric chloride reconverts it into dichloronaphthoquinone (Graebe, *Ann. Ch. Pharm.* cxlix. 5).

Dichlorodiacetoxynaphthol, $C^{10}H^{4}Cl^{2}(OC^{2}H^{3}O)^{2}$, is formed by heating dichloroxynaphthol with acetyl chloride. After washing and recrystallisation from alcohol, it forms long, colourless, silky needles melting at 236° and subliming in long prisms. It is insoluble in water, dissolves slightly in cold alcohol, easily in hot alcohol and ether. It is not attacked by potash, or oxidised by ferric chloride (Graebe, *loc. cit.*).

Chloro-dioxynaphthalic Acid.



$C^{10}H^{7}ClO^{5} = C^{8}H^{4}\left\{\begin{array}{l}Cl\\ OH\\ (CO^{2}H)^{2}\end{array}\right.$ (Th. Hermann, *Ann. Ch. Pharm.* cli. 63; *Zeitschr. f. Chem.* [2] iv. 551; *Jahresb.* 1868, p. 382).—This acid is obtained, together with other products, by adding potassium chlorate in small portions to a mixture of moderately strong sulphuric acid and naphthalene, whereby chlorous acid is evolved, which then acts upon the naphthalene in the manner shown by the equation:

$$C^{10}H^8 + 3ClHO^2 = 2HCl + H^2O + C^{10}H^7ClO^5.$$

The product of the reaction consists of a liquid and a yellowish-red buttery mass. The liquid is decanted; the buttery mass repeatedly exhausted with warm water, as long as acid extracts are obtained; the acid liquid is repeatedly exhausted with ether; the ether evaporated; the residue is digested with benzol; the residue left after evaporation of the benzol is exhausted with warm water; and the solution is decolorised with animal charcoal. This solution when left to evaporate deposits the chlorinated acid in oily drops; these are dissolved in benzol, and the solution is left to evaporate in an open vessel. The syrupy liquid thus obtained gradually deposits crystals of phthalic acid, which may be removed by precipitating the very dilute solution with basic lead acetate; and the remaining liquid, freed from lead and again left to evaporate, yields the chlorinated acid. This, when dried over sulphuric acid, is an amorphous slightly coloured substance, moderately soluble in water, easily soluble in alcohol, ether, and benzol. When boiled with water, it very readily exchanges its chlorine for hydroxyl, so that it is not easily prepared in any considerable quantity.

Dioxynaphthalic Acid. $C^{10}H^8O^6 = C^8H^4\left\{\begin{matrix}(OH)^2\\(COOH)^2\end{matrix}\right.$ (Hermann, *loc. cit.*).—Produced by boiling the chlorinated acid with water, or more readily with baryta-water. It is most easily purified by converting it several times into the acid barium salt. When first separated from this salt, it forms a viscid substance, which however, when left at rest for some time, or more quickly if rubbed with a glass rod, begins to crystallise, and solidifies in a few days to a radio-crystalline mass. According to Carius, the crystals are moderately oblique monoclinic prisms, tabular from predominance of the face $\infty P\infty$. The acid is extremely soluble in water, alcohol, and ether; insoluble in benzol. The solution has a strong acid reaction, decomposes carbonates, and reduces silver from the ammoniacal solution of the nitrate at the boiling heat. Nitric acid oxidises it to phthalic acid. When heated it softens below 100°, melts at 126°, and does not resolidify till cooled to a much lower temperature. Heated between watch-glasses, it yields a sublimate of a sparingly soluble acid and a brown residue which at a higher temperature gives off yellow strong-smelling vapours, condensing partly in the crystalline form, partly in oily drops. Heated to 180° with hydriodic acid of 50 p. c., it yields, with separation of iodine, but without evolution of carbon dioxide, a somewhat sparingly soluble acid, which crystallises in rhombic prisms, sublimes like benzoic acid, forms a yellow precipitate with ferric chloride, and in neutral solution, white precipitates with lead and silver salts.

Dioxynaphthalic acid is bibasic. Most of its salts are easily soluble in hot water. The acid salts crystallise more readily than the neutral salts. Lead acetate produces in the cold solution of the neutral barium salt a precipitate easily soluble in acetic acid; ferric chloride forms a yellow-brown precipitate even in the acid solution. The following dioxynaphthalates have been examined:

$C^{10}H^6O^6K^2$,	very deliquescent, microscopic, rhombic prisms.
$C^{10}H^7O^6K + H^2O$,	spherical groups of needles, or rhombic prisms or pyramids.
$C^{10}H^7O^6(NH^4)$,	slender needles.
$C^{10}H^6O^6Ba + 3H^2O$,	rhombic prisms; anhydrous at 110°.
$(C^{10}H^7O^6)^2Ba$,	monoclinic prisms, or nodular groups of needles.
$(C^{10}H^6O^6)^2Ca(NH^4)^2 + 2H^2O$,	many-sided monoclinic prisms; anhydrous at 120°; decomposing at 140°.
$(C^{10}H^6O^6)^2Ca(NH^4)^2$,	shining monoclinic prisms.
$(C^{10}H^6O^6)^2Cu(NH^4)^2$,	blue rhombic prisms.
$(C^{10}H^6O^6)^4Cu^3H^2 + 2H^2O$,	microscopic monoclinic prisms, obtained by double decomposition of the acid barium salt.
$C^{10}H^6O^6Pb$,	white amorphous precipitate.
$4C^{10}H^6O^6Pb.PbH^2O^2 + 4H^2O$,	monoclinic tables, obtained by boiling the neutral salt with excess of lead acetate.

The solution of this last salt in hot water containing a few drops of nitric acid deposits on cooling, monoclinic prisms of the salt $(C^{10}H^6O^6)^{12}Pb^7H^{10} + 16H^2O$.

Dioxynaphthalic chloride, $C^{10}H^6O^4Cl^2$ or $C^8H^4\left\{\begin{matrix}Cl^2\\(COOH)^2\end{matrix}\right.$, is formed by the action of phosphorus pentachloride on potassium dioxynaphthalate. It is an oily liquid decomposed by water with reproduction of the acid, and by alcohol with formation of diethylic dioxynaphthalate, $C^{10}H^{6}O^{4}.(C^{2}H^{5})^{2}$.

NAPHTHYL CYANIDE. $C^{10}H^{7}CN$.—Syn. with MONOCYANONAPHTHALENE (p. 847).

NAPHTHYL ETHERS. Naphthyl Acetates or **Acetyl-naphthols,** $C^{10}H^{7}(C^{2}H^{3}O)O$, are obtained by treating naphthol with acetyl chloride in a retort with upright condenser ultimately at a gentle heat, distilling off the excess of acetyl chloride, dissolving the residue in alcohol, and evaporating. α *Acetyl-naphthol* washed with water and dried in a vacuum over caustic potash forms a clear, yellowish, oily, nearly inodorous liquid, insoluble in water, easily soluble in alcohol, ether, and chloroform. When it is distilled with aqueous vapour, or even when its alcoholic solution is evaporated over the water-bath, it is resolved into naphthol and acetic acid. β *Acetyl-naphthol* crystallises from its alcoholic solution by evaporation at a gentle heat. When purified by repeated crystallisation from alcohol, and dried in a vacuum over caustic potash, it forms small, soft, shining, needle-shaped crystals having a faint but agreeable odour of anise, easily soluble in alcohol, ether, and chloroform, but insoluble in water. Melts at 60°. Decomposed by heat, like the α ether (Schäffer).

Naphthyl Benzoates or **Benzoyl-naphthols,** $C^{10}H^{7}(C^{7}H^{5}O)O$, are obtained by heating naphthol with benzoyl chloride. The α compound separates from solution in ether by evaporation as a yellowish oil which solidifies after a few days to a crystalline mass, and when recrystallised from ether-alcohol forms large shining tables and prisms melting at 56°. It dissolves in boiling alcohol, and separates on cooling as an oil which soon solidifies to a crystalline mass. By heating with sulphuric acid it is resolved into benzoic and naphthyl-sulphurous acids. β *Benzoyl-naphthol* is sparingly soluble in ether, easily in boiling alcohol, and crystallises therefrom on cooling in nodular groups of slender needles melting at 107°. By heating with alcoholic potash it is resolved into benzoic acid and β naphthol (Maikopar).

Naphthyl Ethylates or **Ethyl-naphthols,** $C^{10}H^{7}(C^{2}H^{5})O$, are produced by heating naphthol with an equivalent quantity of potassium hydrate and excess of ethyl iodide in alcoholic solution, in a retort with upright condenser. On separating the potassium iodide thereby formed, and expelling the alcohol, ethyl-naphthol remains, and may be distilled over with vapour of water.

α Ethyl-naphthol is a yellowish oily liquid which has a peculiar odour, sinks in water, boils at 272° (corr. 280·7°), and does not solidify at −5°. β Ethyl-naphthol is at ordinary temperatures a nearly colourless crystalline mass having an agreeable odour like that of pine-apples. It melts at 33°; dissolves easily in alcohol, ether, chloroform, and benzol, but is insoluble in water (Schäffer).

Naphthyl Phosphate, $PO^{4}(C^{10}H^{7})^{3} = PO(C^{10}H^{7}O)^{3} = \left.\begin{matrix}(PO)'''\\(C^{10}H^{7})^{3}\end{matrix}\right\}O^{3}$ (Schäffer, *Ann. Ch. Pharm.* clii. 289).—Produced by gently heating naphthol with an equivalent quantity of phosphorus pentachloride, and purified by solution in alcohol, decoloration with animal charcoal, and repeated crystallisation. The formation of the phosphate is probably preceded by that of the monochloride; thus:

$$C^{10}H^{7}OH + PCl^{5} = C^{10}H^{7}Cl + HCl + POCl^{3}$$

and

$$3C^{10}H^{7}OH + POCl^{3} = PO(C^{10}H^{7}O)^{3} + 3HCl.$$

α Naphthyl phosphate forms small colourless crystals, easily soluble in ether and chloroform, sparingly soluble in alcohol, insoluble in water. Melting point 145°.

β Naphthyl phosphate crystallises in small white inodorous needles, easily soluble in ether and chloroform, sparingly in cold, easily in hot alcohol; insoluble in water. Melting point 108° nearly.

Naphthyl-sulphuric Acids. $C^{10}H^{8}SO^{4} = C^{10}H^{6}\left\{\begin{matrix}OH\\SO^{3}H\end{matrix}\right. = \left.\begin{matrix}C^{10}H^{7}\\(SO^{2})''\\H\end{matrix}\right\}O^{2}$ (Schäffer, *Ann. Ch. Pharm.* clii. 293).—Produced by heating naphthol with strong sulphuric acid in the water-bath till it is completely dissolved and is no longer precipitated by water, then diluting with water, boiling, and neutralising with lead carbonate. The resulting lead salt, purified by recrystallisation and decomposed by hydrogen sulphide, yields a solution of the acid which may be crystallised by evaporation over the water-bath, and finally in a vacuum over sulphuric acid.

Trithallious Phosphate, $Tl^3(PO^4)$, separates in the crystalline form, even from very dilute neutral solutions of thallious salts, on addition of sodium phosphate and a drop of ammonia, but only when the solution is free from ammoniacal salts, in which it is very soluble (Carstanjen, *Jahresb.* 1867, p. 280).

Zinc Salts.—*Zinc-ammonium phosphate*, $Zn(NH^4)PO^4 + H^2O$. When a solution of 64 grm. zinc sulphate and 100 grms. of aqueous phosphoric acid (strength 16 p. c.) in a large quantity of water is mixed with sufficient ammonia to redissolve the precipitate at first produced, and the liquid is left to itself in a shallow basin, the double salt separates as the ammonia evaporates, in closely adhering crusts composed of microscopic rectangular tables. A very similar salt is produced by slowly evaporating a strongly ammoniacal solution of sodium phosphate and zinc phosphate, but it always contains sodium. A moderately dilute solution of 64 grms. zinc sulphate and 100 grms. of 16 p. c. phosphoric acid exposed for some weeks in a covered basin to a winter temperature, deposits indistinct microscopic crystals, having when air-dried the composition $3P^2O^5.4(NH^4)^2O.6ZnO$ or $\left.\begin{matrix}6(PO)'''\\(NH^4)^8Zn^6\end{matrix}\right\}O^{19}$ (Heintz, *Zeitschr. f. Chem.* [2] iv. 16; see also Schweikert, *ibid.* 306). *Zinc-sodium phosphate*, $ZnNaPO^4$, is produced, by melting microcosmic salt with zinc oxide in the proportions required by the formula, as a transparent colourless mass, which becomes enamel-white on cooling. is not altered by exposure to the air, does not take up water when immersed in it, does not give up soda to water, either cold or boiling, and is insoluble in both (Scheffer, *ibid.* iv. 288).

PYROPHOSPHATES. $\overset{'}{M}{}^4P^2O^7$ or $\overset{''}{M}{}^2P^2O^7$ or $\overset{'''}{M}{}^4P^6O^{21}$ (Gladstone, *Chem. Soc. J.* [2] v. 435).—These salts are produced, not only by the action of heat on the orthophosphates, but likewise by treating phosphoric anhydride with a caustic alkali in alcoholic solution:

$$P^2O^5 + 4KHO = 2H^2O + K^4P^2O^7;$$

also by decomposing phosphorus oxychloride with a moderately concentrated solution of potash or ammonia:

$$2POCl^3 + 5KHO = 5KCl + HCl + H^4P^2O^7.$$

By the action of anhydrous potassium oxide or ammonia sesquicarbonate on the oxychloride, a metaphosphate appears to be produced:

$$POCl^3 + 2K^2O = 3KCl + KPO^3.$$

The white precipitate formed on adding ferric chloride to a solution of sodium pyrophosphate continues to redissolve till $\frac{1}{3}$ mol. ferric chloride, Fe^2Cl^6, has been added to 1 mol. of the pyrophosphate $Na^4P^2O^7$. On further addition of the ferric salt, the precipitate becomes permanent, and when $\frac{2}{3}$ mol. has been added, the precipitation is complete, the precipitate redissolving however in a large excess of ferric chloride. This salt has the composition $(Fe^4)^{xii}P^6O^{21} + 9H^2O$, previously determined by Schwarzenberg (iv. 565). The soluble *sodio-ferric salt* appears to have the composition $Fe^2Na^6P^6O^{21}$, but is difficult to obtain pure. *Cupric salts* form in like manner with sodium pyrophosphate a green precipitate of the salt $Cu^2P^2O^7 + 2H^2O$, soluble with deep blue colour in excess of the sodium salt. The *ferrous*, *zinc*, *mercurous*, *lead*, and *silver salts* are likewise soluble in excess of the sodium salt, the *mercuric* and *chromic salts* insoluble. The normal pyrophosphates of the heavy metals are not altered by boiling with water or neutral saline solutions; they are soluble in dilute acids, and are at first precipitated from their solution in sodium pyrophosphate by sulphuric acid, but are redissolved by an excess of it. Some of them (the ferrous, ferric, cupric, and zinc salts, but not the lead, mercurous, or chromic salts) are precipitated from this solution containing the smallest possible quantity of free acid, by heat, with their original composition but with altered properties, being then soluble in ammonia, but not in sodium pyrophosphate, dilute sulphuric acid, or the original metallic salt (chloride, sulphate, &c.). Gladstone regards these abnormal pyrophosphates as allotropic modifications, which do not appear to exist in free pyrophosphoric acid or in the pyrophosphates of the alkali-metals, inasmuch as the abnormal cupric salt decomposed by hydrogen sulphide yields ordinary pyrophosphoric acid, and the abnormal ferric salt decomposed by caustic potash yields the ordinary potassium salt. The reaction of the ferric salt may be used for the detection of pyrophosphoric acid, namely by adding a few drops of ferric chloride to the solution of the salt, either neutral or prepared with the smallest possible quantity of cold sulphuric acid, redissolving the resulting precipitate in the smallest possible quantity of sulphuric acid, and heating the liquid to the boiling point, whereupon, if pyrophosphoric acid is present, a white flocculent or gelatinous precipitate is formed.

Pyrophosphoric acid may be distinguished from ortho- and meta-phosphoric acids by means of a solution of *leuteo-cobaltic chloride*, which produces in solutions of alkaline pyrophosphates a reddish-yellow precipitate, immediately in moderately dilute solutions, only on agitation in case of great dilution (C. D. Braun, *Zeitschr. anal. Chem.* iii. 468).

PHOTENE. Fritzsche's name for pure anthracene (p. 176).

PHOTERYTHRINE. See the next article.

PHOTOCYANINE. A blue colouring matter produced by the action of oxidising agents in sunshine on cyanine or chinoline-blue (p. 430). It is most abundantly produced by agitating a mixture of 10 pts. concentrated alcoholic solution of cyanine and 100 pts. water at ordinary temperatures with 3 or 4 pts. lead dioxide, till it is decolorised, exposing the clear filtered liquid to the sun till it has acquired a deep blue colour, filtering again, exposing the filtrate to sunshine, and repeating this treatment five or six times. The presence of a small quantity of acid or alkali interferes with the formation of photocyanine. This substance is gradually bleached by ozone; by exposure to light it is decomposed more quickly than cyanine, and finally converted into soluble red photerythrine, or in absence of oxygen into an analogous brown-red colouring matter. Photocyanine is likewise converted into photerythrine by repeatedly treating its alcoholic solution with aqueous chlorine, bromine, or iodine, and then with reducing agents, or by exposing it to sunshine or even to diffused daylight. The solution of photerythrine has a colombo-red colour, not altered by dilute alkalis, but changed to violet by dilute acids. It is likewise decolorised by ozone, chlorine-water, &c., and then reddened again by sunshine (not by reducing agents) with continually diminished intensity of colour, till the whole of the colouring matter is destroyed. The soluble colouring matter produced from photocyanine by the action of sunlight in absence of oxygen exhibits similar reactions (Schönbein, *Ann. Ch. Phys.* [4] vii. 462; *Jahresb.* 1865, p. 424).

PHRAGMITES. The ash of different organs of the common reed (*Phragmites communis*) has been analysed by J. Fittbogen (*Jahresb.* 1865, p. 639).

PHTHALIC ACID. $C^8H^6O^4 = C^6H^4\left\{\begin{matrix}COOH\\COOH\end{matrix}\right.$. *Monocarbobenzoic Acid. Dicarbobenzolic Acid.*—This bibasic acid, derived from benzene by substitution of 2 at. carboxyl for 2 at. hydrogen, is susceptible of three modifications, according to the relative positions of the two carboxyl-groups; namely:

Orthophthalic	Metaphthalic	Paraphthalic
1 : 2	1 : 3	1 : 4

The first of these is the phthalic acid described in vol. iv. p. 628, as produced by oxidation of naphthalene, alizarin, purpurin, and munjistin; the second, also called isophthalic acid, is formed by oxidation of meta-xylene or iso-xylene (p. 293); the third is terephthalic acid, produced by oxidation of turpentine oil, cuminic acid, cuminic aldehyde, xylene, and other aromatic hydrocarbons (v. 724).

1. *Orthophthalic*, or simply *Phthalic acid*, is also produced: α. Together with benzoic acid, formic acid, and carbon dioxide, by oxidising benzene with manganese dioxide and sulphuric acid, its formation being due to the combination of benzoic acid with formic acid, and simultaneous oxidation:

$$\underset{\text{Benzoic}}{C^6H^5.COOH} + \underset{\text{Formic}}{HCOOH} + O = H^2O + \underset{\text{Phthalic}}{C^6H^4(COOH)^2}$$

(Carius, *Zeitschr. f. Chem.* [2] iv. 705).

β. Together with carbon dioxide, by oxidising naphthalene with manganese dioxide and sulphuric acid; and together with dinaphthyl and a brown resinous body, by treating naphthalene with potassium dichromate and sulphuric acid (Lossen, *Ann. Ch. Pharm.* cxliv. 71; see page 844).—γ. Together with carbon dioxide, and several additive and substitution products, by the action of chlorous acid on naphthalene (Hermann, *Zeitschr. f. Chem.* [2] iv. 551; see page 844).

Phthalic acid crystallises from aqueous solution in shining monoclinic crystals, and by slow evaporation in very large, prismatic, radially united forms, with rounded summits; by cooling of the hot solution in small tables (Carius). According to Scheibler (*Zeitschr. f. Chem.* [2] iv. 719), the crystals are rhombic prisms, exhibiting the combination $\infty P . oP . \infty\bar{P}\infty . \bar{P}\infty$. It melts at 170°–180° (Carius), at 184° (Lossen).

Phthalic acid neutralised with sodium carbonate and treated with *sodium-amalgam*, is converted into hydrophthalic acid, $C^8H^8O^4$ (Graebe a. Born; *vid. inf.*). Heated with *sino-dust*, it is reduced to benzoic aldehyde (Baeyer, *Jahresb.* 1866, p. 573).

Heated with 80 pts. saturated *hydriodic acid*, it yields **heptane**, C^7H^{16}, and a small quantity of **octane**, C^8H^{18}:

$$C^8H^6O^4 + 14HI = C^7H^{16} + CO^2 + 2H^2O + 7I^2$$
$$C^8H^6O^4 + 20HI = C^8H^{18} + 4H^2O + 10I^2.$$

Terephthalic acid treated in a similar manner yields only heptane (Berthelot).

Metallic Phthalates.—A solution of phthalic acid half neutralised with baryta-water and evaporated, yields rhombic prisms of the *acid barium salt*, $(C^8H^5O^4)^2Ba$. This salt dissolves in hot water, and gives off at 150°–200° such a quantity of phthalic acid that the residue has nearly the composition $(C^8H^4O^4)^6Ba^5H^2$. The same salt is obtained in crystalline crusts when a solution of the acid neutralised with baryta-water is left to evaporate. The *neutral calcium salt*, $C^8H^4O^4Ca + H^2O$, is obtained by spontaneous evaporation in shining rhombic prisms which give off their water at 160°. The *cupric salt*, $C^8H^4O^4Cu + H^2O$, prepared by adding cupric sulphate to phthalic acid neutralised with baryta-water, is easily soluble in hot water, and crystallises in shining rhombic prisms, which give off their water at 160° (Hermann, *Ann. Ch. Pharm.* cli. 78).

Ethyl Phthalate, $C^8H^4O^4.(C^2H^5)^2$, may be obtained by passing hydrochloric acid gas into an alcoholic solution of phthalic acid; when purified it is a colourless inodorous oil, boiling at 288° (corr. 295°) (Graebe a. Born, *Jahresb.* 1866, p. 411).

On *Chlorophthalic* and *Nitrophthalic acid*, see Faust (*Zeitschr. f. Chem.* [2] v. 107).

2. ***Metaphthalic*** or ***Isophthalic acid*** is produced by the oxidising action of potassium dichromate and sulphuric acid on meta-xylene (p. 293), and separates from the filtered solution in slender needles an inch long, which melt above 300°, and volatilise without blackening. Its crystalline character distinguishes it from terephthalic acid, which is an amorphous powder. The barium and calcium salts of metaphthalic acid form long needle-shaped crystals, very soluble in water (Fittig a. Velguth, *Zeitschr. f. Chem.* [2] iii. 526. Fittig, *ibid.* v. 20). Metaphthalic acid is also produced by the action of sulphuric acid on hydroprehnitic and hydropyromellitic acids (Baeyer, p. 812).

3. ***Paraphthalic*** or ***Terephthalic acid*** is produced by oxidation of several hydrocarbons (v. 725), and in particular of paraxylene or methyl-toluene by chromic acid mixture (Fittig, *loc. cit.*); in like manner from diethyl-benzene:

$$C^6H^4\begin{cases}C^2H^5\\C^2H^5\end{cases} + O^{12} = 2CO^2 + 4H^2O + C^6H^4\begin{cases}CO^2H\\CO^2H\end{cases}$$

(Fittig a. König, *Jahresb.* 1867, p. 610); and, together with acetic acid, by the action of chromic acid on amyl-toluene:

$$C^6H^4\begin{cases}CH^3\\C^5H^{11}\end{cases} + O^{16} = C^6H^4\begin{cases}CO^2H\\CO^2H\end{cases} + 2C^2H^4O^2 + 2H^2O$$

(Bigot a. Fittig, *ibid.* 668). It is also formed, together with phthalic acid, in the oxidation of benzene by manganese dioxide and dilute sulphuric acid (A. E. Oudemans jun., *Zeitschr. f. Chem.* [2] v. 84); by the action of strong potash-ley at the boiling heat on phenylene cyanide: $C^6H^4(CN)^2 + 4H^2O = 2NH^3 + C^6H^4(CO^2H)^2$ (Irelan, *ibid.* 165); and in very small quantity, together with metaphthalic acid, by the action of sulphuric acid on hydropyromellitic acid (Baeyer).

Terephthalic acid heated with 80 pts. of saturated aqueous *hydriodic acid* yields heptane as sole product (p. 696).

On the crystallisation of ethyl terephthalate, see Oudemans (*loc. cit.*).

Hydrophthalic Acid. $C^8H^8O^4$ (Graebe a. Born, *Ann. Ch. Pharm.* cxlii. 330).—Produced by the action of nascent hydrogen upon phthalic acid. A solution of 1 pt. phthalic acid and 1 pt. crystallised sodium carbonate in 8 pts. of cold water is treated in the cold with sodium-amalgam till (in 8 to 14 days) the precipitate formed in a sample of the liquid dissolves in acetic acid. The brown liquid is then neutralised with hydrochloric acid, filtered to separate a brown substance, and the hydrophthalic acid is separated from the filtrate by further addition of hydrochloric acid.

Hydrophthalic acid purified by recrystallisation, with addition of animal charcoal, forms hard tabular monoclinic prisms (with angles of nearly 100° and 80°), cleaving parallel to the end-face. 100 pts. water dissolve 0·98 pt. of the acid at ordinary temperatures, 7·3 pts. at 100°. It is moderately soluble in alcohol, sparingly in ether; the solutions have a strong acid reaction, and decompose carbonates. *Calcium chloride* forms in concentrated solutions of the acid, especially when warm, a precipitate easily soluble in acids; *ferric chloride* forms with solutions of hydrophthalates a brown, *cupric sulphate* a green, *lead acetate*, neutral or basic, a white precipitate;

the lead precipitate is soluble in acetic acid as well as in excess of the precipitant. *Mercurous salts* form white precipitates, becoming grey at the boiling heat; *mercuric chloride* yields on boiling a precipitate of calomel.

Hydrophthalic acid is bibasic, forming acid and neutral salts, the former crystallising the more easily. The easily soluble *sodium salt* forms spherical groups of shining laminæ. The *neutral barium salt*, $C^8H^6O^4Ba$, separates on evaporation in nacreous crusts, easily soluble in warm, less soluble in cold water. The *acid barium salt*, $(C^8H^7O^4)^2Ba + H^2O$, forms stellate groups of crystals, easily soluble in water, sparingly in alcohol, becoming anhydrous at 120°–130°. The *neutral calcium salt*, $C^8H^6O^4Ca$, and the acid salt, $(C^8H^7O^4)^2Ca$, are slightly soluble in water, and crystallise indistinctly. The *lead salt*, $C^8H^6O^4Pb$, is a crystalline powder nearly insoluble in water, easily soluble in dilute acetic acid. The *silver salt* is a white precipitate, moderately soluble in water, becoming black on boiling, and depositing silver, especially in presence of ammonia.

Decompositions.—1. Hydrophthalic acid heated above 200° gives off water and melts to a yellow liquid, which decomposes partially at a higher temperature, yielding a yellow oily solidifying distillate, from which by recrystallisation from alcohol, phthalic anhydride, $C^8H^4O^3$, is obtained.—2. Heated with *soda-lime* it is resolved into benzene, hydrogen, and carbon dioxide:

$$C^6H^6(CO^2H)^2 = C^6H^6 + 2CO^2 + H^2.$$

3. With *phosphorus pentachloride*, it yields benzoyl chloride, carbon monoxide, hydrochloric acid, and phosphorus oxychloride:

$$C^6H^6(CO^2H)^2 + 2PCl^5 = C^6H^5(COCl) + CO + 3HCl + 2POCl^3.$$

4. Heated with strong *sulphuric acid*, it yields phthalic acid, benzoic acid, and carbon monoxide:

$$C^6H^6(CO^2H)^2 + SO^4H^2 = C^6H^4(CO^2H)^2 + 2H^2O + SO^2$$

and

$$C^6H^6(CO^2H)^2 = C^6H^5(CO^2H) + CO + H^2O.$$

5. A solution of hydrophthalic acid heated with a slight excess of *bromine* yields benzoic acid, hydrobromic acid, and carbon dioxide (with a small quantity of phthalic acid):

$$C^6H^6(CO^2H)^2 + Br^2 = C^6H^5(CO^2H) + 2HBr + CO^2.$$

6. Fused with *potassium hydrate*, it yields benzoic acid, together with hydrogen and carbon dioxide:

$$C^6H^6(CO^2H)^2 = C^6H^5(CO^2H) + H^2 + CO^2.$$

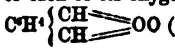
7. By oxidation with dilute *nitric acid* or with *chromic acid*, it is converted into benzoic and phthalic acids.—8. The alcoholic solution of hydrophthalic acid treated with *hydrochloric acid gas*, yields, not hydrophthalate, but benzoate of ethyl, perhaps together with formate, according to the equation:

$$C^6H^6(CO^2)H^2 + 2C^2H^6O = C^6H^5(CO^2C^2H^5) = HCO^2C^2H^5 + 2H^2O.$$

Hydroterephthalic acid, $C^8H^8O^4$, is formed by treating terephthalic acid in moderately soluble concentrated alkaline solution with sodium-amalgam for several days, and separates, on neutralising with hydrochloric acid, as a white flocculent precipitate, quite insoluble in water, and reducing ammoniacal silver solution at the boiling heat (R. Mohs, *Zeitschr. f. Chem.* [2] iii. 68).

PHTHALIC ALDEHYDE, $C^8H^6O^2$, is formed by the action of zinc and hydrochloric acid on phthalic chloride. When dissolved out by ether and purified, it forms a white slightly aromatic substance, melting at 65°, easily soluble in alcohol and ether, slightly soluble in cold, more abundantly in hot water, and crystallising therefrom in small rhombic tables. The warm aqueous solution solidifies with sodium bisulphite to a mass of silky needles (Kolbe a. Wischin, *Chem. Soc. J.* [2] iv. 339).

Phthalic aldehyde is also the chief product formed by the action of magnesium on a solution of phthalic chloride in glacial acetic acid. It volatilises at 180° with vapour of water, and exhibits remarkable stability, perhaps arising from the union of each of its oxygen-atoms with two atoms of carbon, as represented by the formula



$C^6H^4\left\{\begin{matrix}CH\\CH\end{matrix}\right. \gg OO$ (Baeyer, *Zeitschr. f. Chem.* [2] v. 399).

obtained by Chevrier's method is not pure, but may be purified, with loss of a considerable portion, by agitating it with water, separating it as well as possible from the watery liquid, distilling, and rejecting the portion which first passes over at 110°. Chevrier (*ibid.* v. 442) has given several details respecting the properties and reactions of this body, but they are not of much importance.

According to L. Henry (*Deut. chem. Ges. Ber.* ii. 638), the sulphochloride is formed by direct combination of sulphur and the trichloride at 130°. It boils at 125°–128° (compare iv. 606).

Hydrides. According to Rüdorff (*Zeitschr. f. Chem.* [2] ii. 637), the yellow body formed by the action of water on phosphorus di-iodide, commonly regarded as amorphous phosphorus, agrees in its properties with solid phosphorus hydride, P^2H or P^4H^2. On adding phosphorus iodide to hot water, this compound is immediately separated, and non-spontaneously inflammable phosphorus tri-hydride is given off; in cold water the reaction takes place gradually. Rüdorff represents it by the following equation:

$$40PI^3 + 48H^2O = 2P^4H^2 + 4PH^3 + 3P^2O^5 + 11P^2O^3 + 80HI.$$

According to Commaille (*J. Pharm.* [4] viii. 321), the tri-hydride is rapidly evolved by the action of phosphorus on potash-ley even at ordinary temperatures: hence an error may arise in the analysis of gases, when, after treatment of the gas with potash, phosphorus is introduced to absorb oxygen, and comes in contact with the potash.

Oxides and Oxygen-acids of Phosphorus.

Phosphorous Acid. PH^3O^3.—This acid is produced by atmospheric oxidation of hypophosphorous acid. A solution of barium hypophosphite decomposed by sulphuric acid, and exposed for a long time to the air, yielded, when neutralised with calcium carbonate, a precipitate of calcium phosphite (Rammelsberg, *Zeitschr. f. Chem.* [2] iv. 724).

When 1 mol. crystallised phosphorous acid and 1 mol. *bromine* are heated in a sealed tube to 100°, with frequent agitation, hydrobromic and metaphosphoric acids are produced:

$$PH^3O^3 + Br^2 = 2HBr + PHO^3.$$

With 3 mol. bromine to 4 mol. phosphorous acid, the products are orthophosphoric acid, hydrobromic acid, and phosphorus tribromide:

$$4PH^3O^3 + 3Br^2 = 3PH^3O^4 + 3HBr + PBr^3.$$

The action of *iodine* is not exactly analogous to that of bromine. With a small proportion of iodine, phosphorus iodide and metaphosphoric acid are found among the products. With a larger proportion of iodine, the products are orthophosphoric acid, hydriodic acid, phosphonium iodide, and phosphorus di-iodide:

$$8PH^3O^3 + 5I = 6PH^3O^4 + 2HI + PH^4I + PI^2$$

(Gustavson, *Bull. Soc. Chim.* [2] viii. 29). According to Ordinaire (*Compt. rend.* lxiv. 363), 1 mol. phosphorous acid and 2 mol. bromine heated in a sealed tube, form, together with hydrobromic acid, a very deliquescent crystallised body, which he regards as monobromophosphorous acid; it is decomposed by boiling water, with formation of a new gelatinous acid. Dry chlorine at 100° acts in a similar manner. The formation of phosphoric acid was not observed in either case.

METALLIC PHOSPHITES.—The constitution of these salts has been carefully examined by Rammelsberg (*Berl. Akad. Ber.* 1866, p. 537; *Chem. Soc. J.* [2] v. 388; further *Pogg. Ann.* cxxxi. 263, 359; cxxxii. 481; *Jahresb.* 1867, p. 141). His experiments confirm the view advocated by H. Rose (*Pogg. Ann.* viii. 205; ix. 23, 215), that different phosphites contain different quantities of chemically combined or constitutional water, or its elements (exclusive of water of crystallisation), in opposition to that of Wurtz, according to which, all dry phosphites contain the same amount of constitutional water, namely 1 molecule. Rammelsberg does not however regard the existence of the salts $M''HPO^3$ (or $\acute{M}^2H^2P^2O^6$) and $\acute{M}^2H^4P^2O^7$ as demonstrating the existence of two different phosphorous acids, $H^6P^2O^6$ and $H^8P^2O^7$, or the evolution of hydrogen from heated phosphorous acid as a proof that the hydrogen does not exist therein in the form of water. He infers rather, from the whole of the facts observed, that both crystallised phosphorous acid and the metallic phosphites contain water ready formed, but more intimately combined than in other hydrates, so that it is not given off below 200°, and its elements take part in the decomposition of

According to Gobley (*J. Pharm.* [4] ii. 156), narcotine may be extracted from opium—together with a fatty oil and a substance resembling caoutchouc—by digestion with oil of turpentine at 100°.

Narcotine Tri-iodide, $C^{22}H^{23}NO^7HI^3$, is formed by mixing an alcoholic solution of narcotine with hydrochloric acid, adding the calculated quantity of iodine, and then water till a permanent turbidity is produced. On stirring the liquid, the tri-iodide separates in shining laminæ, and an additional quantity may be obtained by adding more water. This compound is moderately soluble in alcohol, but undergoes a remarkable alteration when boiled therewith, the solution on cooling depositing the tri-iodide of a new base, tarconine, $C^{12}H^{11}NO^3$, containing 2 at. hydrogen less than cotarnine:

$$\underset{\substack{\text{Narcotine}\\\text{tri-iodide.}}}{3(C^{22}H^{23}NO^7.HI^3)} + H^2O = \underset{\substack{\text{Tarconine}\\\text{tri-iodide.}}}{C^{12}H^{11}NO^3.HI^3} + \underset{\substack{\text{Opianic}\\\text{acid.}}}{C^{10}H^{10}O^5} + 4HI +$$

$$\underset{\substack{\text{Narcotine}\\\text{Hydriodide.}}}{2(C^{22}H^{23}NO^7.HI)}$$

(Jörgensen, *Deut. chem. Ges. Ber.* 1869, 460; *Zeitschr. f. Chem.* [2] v. 673).

NEPHRITE. For analyses of this mineral from the pile-buildings of the Swiss lakes and other localities, see Fellenberg (*Jahresb.* 1865, p. 880); Damour (*Compt. rend.* lxi. 313, 357; *Jahresb.* 1865, p. 880).

NEPHROZYMASE. This name is applied by Béchamp (*Bull. Soc. Chim.* [2] iii. 213) to a soluble ferment existing in the urine of man, the dog, and the rabbit, and capable of converting starch into sugar.

NEURINE. Syn. with CHOLINE (p. 448).

NICKEL. The atomic weight of this metal has been redetermined by Russell (*Chem. Soc. J.* [2] vii. 294) by measuring the volume of hydrogen evolved on dissolving a known weight of the pure metal in hydrochloric acid. (See ANALYSIS OF GASES, p. 142.) The mean of four closely agreeing experiments gave for the atomic weight of nickel the number 58·70, which is very nearly the same as that which Russell formerly obtained (iv. 40) by reducing the pure monoxide with hydrogen, viz. 58·74.

Different but less trustworthy results have been obtained by Sommaruga (*Jahresb.* 1866, p. 244) and by Winkler (*ibid.* 1867, p. 289). The former, by analysis of niccolo-potassic sulphate, $(SO^4)^2NiK^2 + 6H^2O$, obtained the number 58; the latter, by reducing a neutral solution of sodio-auric chloride with metallic nickel, and weighing the gold precipitated, found Ni = 59·06.

Detection of Nickel.—A solution of a nickel salt mixed with sodium acetate and *hypochlorite*, and heated to the boiling point, deposits a deep blue, nearly black peroxide forming a specular coating on the glass; the reaction is extremely delicate, and every trace of nickel is thereby removed from the liquid (Popp, *Ann. Ch. Pharm.* cxxxi. 363; see also Wicke, *Zeitschr. f. Chem.* [2] i. 86; *Jahresb.* 1865, p. 267). *Sodium hyposulphite* added to nickel salts at the boiling heat throws down black nickel sulphide, probably also forming trithionate and chloride of sodium:

$$NiCl^2 + 2Na^2S^2O^3 = NiS + Na^2S^3O^6 + 2NaCl.$$

The precipitate is not attacked by strong sulphuric or boiling hydrochloric acid, but is oxidised by nitric acid to nickel sulphate (W. Gibbs, *Sill. Am. J.* [2] xxxvii. 346).

Potassium sulphocarbonate colours a nickel solution crimson-brown, or, if very dilute, rose-red. The solution to be tested is first freed from cobalt by potassium nitrite, and the filtrate is made alkaline with ammonia, mixed with sal-ammoniac, and precipitated with a little colourless ammonium sulphide. The filtrate from this precipitate yields, when strongly concentrated by evaporation, a precipitate of nickel sulphide. This precipitate is washed on a filter, dried, ignited, treated with a little nitric acid, and evaporated. The saline residue is dissolved in water and added to about 50 c. c. water containing 1 or 2 drops of the solution of sulphocarbonate (prepared by saturating one half of 250 c. c. potash-ley containing 5 p. c. K^2O with hydrogen sulphide, adding the other half, gently warming the liquid for two days with 10 c. c. carbon bisulphide, and then decanting from the uncombined CS^2). If nickel is present, the rose-red or crimson colour will be produced. This reaction suffices to distinguish $\frac{1}{100}$ milligrm. of nickel in 1 c. c. of liquid. The nickel-compound dissolved in the alkaline sulphocarbonate exhibits in dilute solution distinct absorption-bands; concentrated solutions stop the light almost completely (C. D. Braun, *Zeitschr. f. Chem.* [2] v. 309).

Acid Phosphites.—A solution of the normal barium salt in the requisite quantity of phosphorous acid yields, by spontaneous evaporation, radiate groups of white silky needles of the salt $Ba^2H^2P^2O^6.3H^3PO^3 + 2H^2O$. A solution of 1 mol. of the normal salt in rather more than 2 mol. phosphorous acid, yields crystals, not of the biacid, but of the *sesqui-acid salt*, $Ba^2H^2P^2O^6.H^3PO^3 + 8H^2O$, which melts when heated and gives off hydrogen phosphide at 250°. The *biacid salt* crystallises from the solution of the two preceding salts by evaporation over sulphuric acid, with an amount of water corresponding to the formula $BaH^4P^2O^6 + 2H^2O$; ammonia added to the aqueous solution of this salt throws down, not an acid salt as supposed by Rose, but the normal salt. *Zinc Salts.*—By dissolving the neutral zinc salt in phosphorous acid, Rammelsberg obtained various crystallised compounds corresponding to the formulæ $Zn^2H^5P^3O^9 + H^2O$, $Zn^3H^9P^5O^{15} + H^2O$, and $Zn^2H^{11}P^5O^{15}$. An *acid uranic phosphite*, $(UO)^2H^2P^2O^6 + 6H^2O$, is obtained, by adding recently precipitated ammonium uranate to the aqueous solution of phosphorus trichloride, as a gradually formed yellow precipitate, which on exposure to the air dries up to hard translucent lumps.

Phosphorous Ethers.—Rammelsberg represents these ethers by formulæ analogous to those of the acid metallic phosphites as follows;

$\left\{\begin{matrix}H^4P^2O^5\\H^2O\end{matrix}\right.$ Phosphorous acid.	$\left\{\begin{matrix}H^2BaP^2O^5\\H^2O\end{matrix}\right.$ Acid barium phosphite.
$\left\{\begin{matrix}(C^2H^5)^4P^2O^5\\H^2O\end{matrix}\right.$ Ethylic phosphite.	$\left\{\begin{matrix}H^2(C^2H^5)^2P^2O^5\\H^2O\end{matrix}\right.$ Ethylphosphorous acid.
$\left\{\begin{matrix}(C^2H^5)^4P^2O^5\\(C^2H^5)^2O\end{matrix}\right.$ Triethylic phosphite.	$\left\{\begin{matrix}Ba(C^2H^5)^2P^2O^5\\H^2O\end{matrix}\right.$ Barium ethylphosphite.

Phosphoric Anhydride, Acid, and **Salts.** On the preparation of phosphoric anhydride on the large scale, see Grabowski (*Ann. Ch. Pharm.* cxxxvi. *119*; *Jahresb.* 1865, p. 135).

Mich. Pettenkofer (*Ann. Ch. Pharm.* cxxxviii. 57; *Jahresb.* 1866, p. 138) describes a method of preparing phosphoric acid, simultaneously with hydriodic acid, by treating ordinary phosphorus with iodine and water, distilling off the hydriodic acid, and oxidising the residue, which contains phosphorous and phosphoric acids, with nitric acid.

According to Krämer (*Zeitschr. f. Chem.* [2] v. 543), phosphoric acid may be obtained in transparent prismatic crystals, by evaporating from an aqueous solution, the strength of which is known from its specific gravity, such a quantity of water that the residual liquid shall have exactly the composition H^3PO^4; the acid then crystallises on cooling.

In the purest so-called glacial phosphoric acid of commerce, Brescius (*Zeitschr. anal. Chem.* vi. 187) found 15·3 p. c. soda. He finds that really pure phosphoric acid forms only a soft glutinous mass.

The following table of the relations between the specific gravity and strength of aqueous phosphoric acid (prepared by oxidising amorphous phosphorus with nitric acid) is given by J. Watts (*Chem. News*, xii. 160):

Spec. Grav.	p. c. P^2O^5	Spec. Grav.	p. c. P^2O^5	Spec. Grav.	p. c. P^2O^5	Spec. Grav.	p. c. P^2O^5
1·508	49·60	1·369	39·21	1·236	27·30	1·095	12·18
1·492	48·41	1·356	38·00	1·226	26·36	1·081	10·44
1·476	47·10	1·347	37·37	1·211	24·79	1·073	9·53
1·464	45·63	1·339	36·74	1·197	23·23	1·066	8·62
1·453	45·38	1·328	36·15	1·185	22·07	1·056	7·39
1·442	44·13	1·315	34·82	1·173	20·91	1·047	6·17
1·434	43·95	1·302	33·49	1·162	19·73	1·031	4·15
1·426	43·28	1·293	32·71	1·153	18·81	1·022	3·03
1·418	42·61	1·285	31·94	1·144	17·89	1·014	1·91
1·401	41·60	1·276	31·03	1·136	16·95	1·006	0·790
1·392	40·86	1·268	30·13	1·124	15·64		
1·384	40·12	1·257	29·16	1·113	14·33		
1·376	39·66	1·247	28·24	1·109	13·25		

Estimation of Phosphoric Acid.—1. The conditions under which phosphoric acid is most completely precipitated by *ammonium molybdate* have been examined by Fresenius (*Zeitschr. anal. Chem.* iv. 151): α. The estimation of phosphoric acid by precipitation with ammonium molybdate is in itself an exact method.—β. Nitric acid, even if present in very large excess, does not interfere with its accuracy.—γ. Hydrochloric acid, if present in somewhat considerable quantity, prevents the precipitation wholly or partially; when its quantity is reduced to about 3·3 p. c. of the liquid, the results, though still too low, begin to approach the truth.—δ. If a large quantity of nitric acid is also present, a somewhat considerable quantity of hydrochloric acid is still more prejudicial, 3·3 p. c. of it in that case completely preventing the precipitation.—ε. Sulphuric acid, ferric chloride, and aluminium chloride, even in considerable quantity, do not interfere with the precipitation.—ζ. In presence of a large quantity of sal-ammoniac, the results are somewhat too low; they also become less exact as the solution is more diluted with water.

2. According to E. Fleischer (*Zeitschr. anal. Chem.* vi. 28), aluminium phosphate, like aluminium hydrate, is slightly soluble in ammonia, so that on mixing the solution of a phosphate with a slight excess of an aluminium salt, and then supersaturating with ammonia, part of the phosphoric acid remains in solution. But in neutral solutions, or in presence of a slight excess of acetic acid, phosphoric acid is completely precipitated by aluminium salts, if not added in great excess, the precipitate having the composition $\mathrm{Al^2O^3.P^2O^5}$. Phosphoric acid may be estimated volumetrically in a solution acidulated with acetic acid by means of a one-tenth normal solution of potash-alum (containing 5·15 grm. alumina in a litre), the end of the precipitation being indicated by adding an alcoholic solution of brazilin, which is coloured distinctly blue by aluminium acetate, even in very dilute solution (Fleischer, *Zeitschr. anal. Chem.* iv. 355; *Jahresb.* 1865, p. 707; 1867, p. 844).

According to Schweikert (*Jahresb.* 1867, p. 847), phosphoric acid cannot be completely separated from zinc oxide by fusion with sodium carbonate, since part of the phosphoric acid remains with the zinc, and part of the latter remains dissolved as sodium zincate.

Schloesing (*Compt. rend.* lxvi. 1043; *Zeitschr. f. Chem.* [2] iv. 567) estimates phosphoric acid in phosphates by converting them into iron phosphide. This is effected by mixing the phosphate with an iron silicate,* charcoal, and, if the phosphate does not contain excess of base, also with metallic iron. This mixture is ignited in a charcoal-lined crucible by means of a powerful gas-blowpipe; the fused mass is pulverised; and the metallic iron phosphide separated from the granules is heated in a glass tube through which a stream of chlorine is passed. The phosphorus then passes over as trichloride, which is received in water, and the resulting phosphorous acid is oxidised by nitric acid to phosphoric acid, which is estimated by the ordinary methods.

On the estimation of phosphoric acid in phosphorite, see Fresenius (*Zeitschr. anal. Chem.* vi. 403; *Jahresb.* 1867, p. 835); in superphosphate, coprolites, plant-ashes, soils, manures, &c., see G. Jones (*Chem. News*, xii. 13); W. Arnot (*ibid.* xi. 49); R. Warington jun. (*ibid.* xii. 209); Fresenius (*Zeitschr. anal. Chem.* vii. 304; *Jahresb.* 1868, p. 858); Schloesing (*Zeitschr. f. Chem.* [2] v. 156); De Gasparin (*Compt. rend.* lxviii. 1176; *Zeitschr. f. Chem.* [2] v. 444).

ORTHOPHOSPHATES.—On the reactions of *tricalcic phosphate* with calcium chloride and sulphuric acid, see Piccard (*Zeitschr. f. Chem.* [2] ii. 545; iii. 187; *Jahresb.* 1866, p. 168; 1867, p. 909).

Cupric Salts.—The precipitate formed on adding 2 mol. ordinary sodium phosphate to a dilute solution of 3 mol. cupric sulphate has, when air-dried, the composition $\overset{\prime\prime}{\mathrm{Cu}}{}^4\mathrm{H(PO^4)^3 + 5H^2O}$. Rammelsberg (*Pogg. Ann.* lxviii. 388), probably by drying it at a higher temperature, obtained it with 3 mol. water. When this precipitate is boiled with very dilute ammonia, small dark blue crystals, sparingly soluble in water and alcohol, separate on cooling. By boiling the same precipitate with ammonia, placing upon this liquid a layer of alcoholic solution of ammonia, leaving it for several weeks, and promoting the diffusion by frequent gentle agitation, sky-blue crystals separate, consisting of *ammonio-cupric phosphate*, $\left.\begin{matrix}\mathrm{Cu''}\\ \mathrm{(NH^4)^7}\end{matrix}\right\}\mathrm{(PO^4)^3 + 7H^2O}$. These crystals are monoclinic prisms with oblique end-faces inclined 65° to the principal axis. They dissolve easily in cold water, smell strongly of ammonia, and give it up for the most part even at ordinary temperatures, crumbling to a bluish-white powder (Metzner, *Ann. Ch. Pharm.* cxlix. 66; *Zeitschr. f. Chem.* [2] v. 250).

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* The iron silicate is prepared by fusing together 28 pts. iron-filings, 80 pts. ferric oxide, and 48 pts. pure sand, separating the fused mass from the excess of iron, and pulverising.

Trithallious Phosphate, $Tl^3(PO^4)$, separates in the crystalline form, even from very dilute neutral solutions of thallious salts, on addition of sodium phosphate and a drop of ammonia, but only when the solution is free from ammoniacal salts, in which it is very soluble (Carstanjen, *Jahresb.* 1867, p. 280).

Zinc Salts.—*Zinc-ammonium phosphate*, $Zn(NH^4)PO^4 + H^2O$. When a solution of 64 grm. zinc sulphate and 100 grms. of aqueous phosphoric acid (strength 16 p. c.) in a large quantity of water is mixed with sufficient ammonia to redissolve the precipitate at first produced, and the liquid is left to itself in a shallow basin, the double salt separates as the ammonia evaporates, in closely adhering crusts composed of microscopic rectangular tables. A very similar salt is produced by slowly evaporating a strongly ammoniacal solution of sodium phosphate and zinc phosphate, but it always contains sodium. A moderately dilute solution of 64 grms. zinc sulphate and 100 grms. of 16 p. c. phosphoric acid exposed for some weeks in a covered basin to a winter temperature, deposits indistinct microscopic crystals, having when air-dried the composition $3P^2O^5.4(NH^4)^2O.6ZnO$ or $\left.\begin{matrix}6(PO)'''\\(NH^4)^6Zn^6\end{matrix}\right\}O^{19}$ (Heintz, *Zeitschr. f. Chem.* [2] iv. 16; see also Schweikert, *ibid.* 306). *Zinc-sodium phosphate*, $ZnNaPO^4$, is produced, by melting microcosmic salt with zinc oxide in the proportions required by the formula, as a transparent colourless mass, which becomes enamel-white on cooling. is not altered by exposure to the air, does not take up water when immersed in it, does not give up soda to water, either cold or boiling, and is insoluble in both (Scheffer, *ibid.* iv. 288).

PYROPHOSPHATES. $\overset{\prime}{M}{}^4P^2O^7$ or $\overset{\prime\prime}{M}{}^2P^2O^7$ or $\overset{\prime\prime\prime}{M}{}^4P^6O^{21}$ (Gladstone, *Chem. Soc. J.* [2] v. 435).—These salts are produced, not only by the action of heat on the orthophosphates, but likewise by treating phosphoric anhydride with a caustic alkali in alcoholic solution:

$$P^2O^5 + 4KHO = 2H^2O + K^4P^2O^7;$$

also by decomposing phosphorus oxychloride with a moderately concentrated solution of potash or ammonia:

$$2POCl^3 + 5KHO = 5KCl + HCl + H^4P^2O^7.$$

By the action of anhydrous potassium oxide or ammonia sesquicarbonate on the oxychloride, a metaphosphate appears to be produced:

$$POCl^3 + 2K^2O = 3KCl + KPO^3.$$

The white precipitate formed on adding ferric chloride to a solution of sodium pyrophosphate continues to redissolve till $\frac{1}{8}$ mol. ferric chloride, Fe^2Cl^6, has been added to 1 mol. of the pyrophosphate $Na^4P^2O^7$. On further addition of the ferric salt, the precipitate becomes permanent, and when $\frac{2}{3}$ mol. has been added, the precipitation is complete, the precipitate redissolving however in a large excess of ferric chloride. This salt has the composition $(Fe^4)^{xii}P^6O^{21} + 9H^2O$, previously determined by Schwarzenberg (iv. 565). The soluble *sodio-ferric salt* appears to have the composition $Fe^2Na^6P^6O^{21}$, but is difficult to obtain pure. *Cupric salts* form in like manner with sodium pyrophosphate a green precipitate of the salt $Cu^2P^2O^7 + 2H^2O$, soluble with deep blue colour in excess of the sodium salt. The *ferrous*, *zinc*, *mercurous*, *lead*, and *silver salts* are likewise soluble in excess of the sodium salt, the *mercuric* and *chromic salts* insoluble. The normal pyrophosphates of the heavy metals are not altered by boiling with water or neutral saline solutions; they are soluble in dilute acids, and are at first precipitated from their solution in sodium pyrophosphate by sulphuric acid, but are redissolved by an excess of it. Some of them (the ferrous, ferric, cupric, and zinc salts, but not the lead, mercurous, or chromic salts) are precipitated from this solution containing the smallest possible quantity of free acid, by heat, with their original composition but with altered properties, being then soluble in ammonia, but not in sodium pyrophosphate, dilute sulphuric acid, or the original metallic salt (chloride, sulphate, &c.). Gladstone regards these abnormal pyrophosphates as allotropic modifications, which do not appear to exist in free pyrophosphoric acid or in the pyrophosphates of the alkali-metals, inasmuch as the abnormal cupric salt decomposed by hydrogen sulphide yields ordinary pyrophosphoric acid, and the abnormal ferric salt decomposed by caustic potash yields the ordinary potassium salt. The reaction of the ferric salt may be used for the detection of pyrophosphoric acid, namely by adding a few drops of ferric chloride to the solution of the salt, either neutral or prepared with the smallest possible quantity of cold sulphuric acid, redissolving the resulting precipitate in the smallest possible quantity of sulphuric acid, and heating the liquid to the boiling point, whereupon, if pyrophosphoric acid is present, a white flocculent or gelatinous precipitate is formed.

Pyrophosphoric acid may be distinguished from ortho- and meta-phosphoric acids by means of a solution of *leuteo-cobaltic chloride*, which produces in solutions of alkaline pyrophosphates a reddish-yellow precipitate, immediately in moderately dilute solutions, only on agitation in case of great dilution (C. D. Braun, *Zeitschr. anal. Chem.* iii. 468).

PHOTENE. Fritzsche's name for pure anthracene (p. 176).

PHOTERYTHRINE. See the next article.

PHOTOCYANINE. A blue colouring matter produced by the action of oxidising agents in sunshine on cyanine or chinoline-blue (p. 430). It is most abundantly produced by agitating a mixture of 10 pts. concentrated alcoholic solution of cyanine and 100 pts. water at ordinary temperatures with 3 or 4 pts. lead dioxide, till it is decolorised, exposing the clear filtered liquid to the sun till it has acquired a deep blue colour, filtering again, exposing the filtrate to sunshine, and repeating this treatment five or six times. The presence of a small quantity of acid or alkali interferes with the formation of photocyanine. This substance is gradually bleached by ozone; by exposure to light it is decomposed more quickly than cyanine, and finally converted into soluble red photerythrine, or in absence of oxygen into an analogous brown-red colouring matter. Photocyanine is likewise converted into photerythrine by repeatedly treating its alcoholic solution with aqueous chlorine, bromine, or iodine, and then with reducing agents, or by exposing it to sunshine or even to diffused daylight. The solution of photerythrine has a colombo-red colour, not altered by dilute alkalis, but changed to violet by dilute acids. It is likewise decolorised by ozone, chlorine-water, &c., and then reddened again by sunshine (not by reducing agents) with continually diminished intensity of colour, till the whole of the colouring matter is destroyed. The soluble colouring matter produced from photocyanine by the action of sunlight in absence of oxygen exhibits similar reactions (Schönbein, *Ann. Ch. Phys.* [4] vii. 462; *Jahresb.* 1865, p. 424).

PHRAGMITES. The ash of different organs of the common reed (*Phragmites communis*) has been analysed by J. Fittbogen (*Jahresb.* 1865, p. 639).

PHTHALIC ACID. $C^8H^6O^4 = C^6H^4\left\{\begin{matrix}COOH\\COOH\end{matrix}\right.$. *Monocarbobenzoic Acid. Dicarbobenzolic Acid.*—This bibasic acid, derived from benzene by substitution of 2 at. carboxyl for 2 at. hydrogen, is susceptible of three modifications, according to the relative positions of the two carboxyl-groups; namely:

Orthophthalic	Metaphthalic	Paraphthalic
1:2	1:3	1:4

The first of these is the phthalic acid described in vol. iv. p. 628, as produced by oxidation of naphthalene, alizarin, purpurin, and munjistin; the second, also called isophthalic acid, is formed by oxidation of meta-xylene or iso-xylene (p. 293); the third is terephthalic acid, produced by oxidation of turpentine oil, cuminic acid, cuminic aldehyde, xylene, and other aromatic hydrocarbons (v. 724).

1. *Orthophthalic*, or simply *Phthalic acid*, is also produced: *a.* Together with benzoic acid, formic acid, and carbon dioxide, by oxidising benzene with manganese dioxide and sulphuric acid, its formation being due to the combination of benzoic acid with formic acid, and simultaneous oxidation:

$$\underset{\text{Benzoic}}{C^6H^5.COOH} + \underset{\text{Formic}}{HCOOH} + O = H^2O + \underset{\text{Phthalic}}{C^6H^4(COOH)^2}$$

(Carius, *Zeitschr. f. Chem.* [2] iv. 705).

β. Together with carbon dioxide, by oxidising naphthalene with manganese dioxide and sulphuric acid; and together with dinaphthyl and a brown resinous body, by treating naphthalene with potassium dichromate and sulphuric acid (Lossen, *Ann. Ch. Pharm.* cxliv. 71; see page 844).—*γ.* Together with carbon dioxide, and several additive and substitution products, by the action of chlorous acid on naphthalene (Hermann, *Zeitschr. f. Chem.* [2] iv. 551; see page 844).

Phthalic acid crystallises from aqueous solution in shining monoclinic crystals, and by slow evaporation in very large, prismatic, radially united forms, with rounded summits; by cooling of the hot solution in small tables (Carius). According to Scheibler (*Zeitschr. f. Chem.* [2] iv. 719), the crystals are rhombic prisms, exhibiting the combination $\infty P \,.\, oP \,.\, \infty\bar{P}\infty \,.\, \breve{P}\infty$. It melts at 170°–180° (Carius), at 184° (Lossen).

Phthalic acid neutralised with sodium carbonate and treated with *sodium-amalgam*, is converted into hydrophthalic acid, $C^8H^8O^4$ (Graebe a. Born; *vid. inf.*). Heated with *zinc-dust*, it is reduced to benzoic aldehyde (Baeyer, *Jahresb.* 1866, p. 573).

Heated with 80 pts. saturated *hydriodic acid*, it yields heptane, C^7H^{16}, and a small quantity of octane, C^8H^{18}:

$$C^8H^6O^4 + 14HI = C^7H^{16} + CO^2 + 2H^2O + 7I^2$$
$$C^8H^6O^4 + 20HI = C^8H^{18} + 4H^2O + 10I^2.$$

Terephthalic acid treated in a similar manner yields only heptane (Berthelot).

Metallic Phthalates.—A solution of phthalic acid half neutralised with baryta-water and evaporated, yields rhombic prisms of the *acid barium salt*, $(C^8H^5O^4)^2Ba$. This salt dissolves in hot water, and gives off at 150°–200° such a quantity of phthalic acid that the residue has nearly the composition $(C^8H^4O^4)^6Ba^5H^2$. The same salt is obtained in crystalline crusts when a solution of the acid neutralised with baryta-water is left to evaporate. The *neutral calcium salt*, $C^8H^4O^4Ca + H^2O$, is obtained by spontaneous evaporation in shining rhombic prisms which give off their water at 160°. The *cupric salt*, $C^8H^4O^4Cu + H^2O$, prepared by adding cupric sulphate to phthalic acid neutralised with baryta-water, is easily soluble in hot water, and crystallises in shining rhombic prisms, which give off their water at 160° (Hermann, *Ann. Ch. Pharm.* cli. 78).

Ethyl Phthalate, $C^8H^4O^4.(C^2H^5)^2$, may be obtained by passing hydrochloric acid gas into an alcoholic solution of phthalic acid; when purified it is a colourless inodorous oil, boiling at 288° (corr. 295°) (Graebe a. Born, *Jahresb.* 1866, p. 411).

On *Chlorophthalic* and *Nitrophthalic acid*, see Faust (*Zeitschr. f. Chem.* [2] v. 107).

2. *Metaphthalic* or *Isophthalic acid* is produced by the oxidising action of potassium dichromate and sulphuric acid on meta-xylene (p. 293), and separates from the filtered solution in slender needles an inch long, which melt above 300°, and volatilise without blackening. Its crystalline character distinguishes it from terephthalic acid, which is an amorphous powder. The barium and calcium salts of metaphthalic acid form long needle-shaped crystals, very soluble in water (Fittig a. Velguth, *Zeitschr. f. Chem.* [2] iii. 526. Fittig, *ibid.* v. 20). Metaphthalic acid is also produced by the action of sulphuric acid on hydroprehnitic and hydropyromellitic acids (Baeyer, p. 812).

3. *Paraphthalic* or *Terephthalic acid* is produced by oxidation of several hydrocarbons (v. 725), and in particular of paraxylene or methyl-toluene by chromic acid mixture (Fittig, *loc. cit.*); in like manner from diethyl-benzene:

$$C^6H^4\begin{cases}C^2H^5\\C^2H^5\end{cases} + O^{12} = 2CO^2 + 4H^2O + C^6H^4\begin{cases}CO^2H\\CO^2H\end{cases}$$

(Fittig a. König, *Jahresb.* 1867, p. 610); and, together with acetic acid, by the action of chromic acid on amyl-toluene:

$$C^6H^4\begin{cases}CH^3\\C^5H^{11}\end{cases} + O^{10} = C^6H^4\begin{cases}CO^2H\\CO^2H\end{cases} + 2C^2H^4O^2 + 2H^2O$$

(Bigot a. Fittig, *ibid.* 668). It is also formed, together with phthalic acid, in the oxidation of benzene by manganese dioxide and dilute sulphuric acid (A. E. Oudemans jun., *Zeitschr. f. Chem.* [2] v. 84); by the action of strong potash-ley at the boiling heat on phenylene cyanide: $C^6H^4(CN)^2 + 4H^2O = 2NH^3 + C^6H^4(CO^2H)^2$ (Irelan, *ibid.* 165); and in very small quantity, together with metaphthalic acid, by the action of sulphuric acid on hydropyromellitic acid (Baeyer).

Terephthalic acid heated with 80 pts. of saturated aqueous *hydriodic acid* yields heptane as sole product (p. 696).

On the crystallisation of ethyl terephthalate, see Oudemans (*loc. cit.*).

Hydrophthalic Acid. $C^8H^8O^4$ (Graebe a. Born, *Ann. Ch. Pharm.* cxlii. 330).—Produced by the action of nascent hydrogen upon phthalic acid. A solution of 1 pt. phthalic acid and 1 pt. crystallised sodium carbonate in 8 pts. of cold water is treated in the cold with sodium-amalgam till (in 8 to 14 days) the precipitate formed in a sample of the liquid dissolves in acetic acid. The brown liquid is then neutralised with hydrochloric acid, filtered to separate a brown substance, and the hydrophthalic acid is separated from the filtrate by further addition of hydrochloric acid.

Hydrophthalic acid purified by recrystallisation, with addition of animal charcoal, forms hard tabular monoclinic prisms (with angles of nearly 100° and 80°), cleaving parallel to the end-face. 100 pts. water dissolve 0·98 pt. of the acid at ordinary temperatures, 7·3 pts. at 100°. It is moderately soluble in alcohol, sparingly in ether; the solutions have a strong acid reaction, and decompose carbonates. *Calcium chloride* forms in concentrated solutions of the acid, especially when warm, a precipitate easily soluble in acids; *ferric chloride* forms with solutions of hydrophthalates a brown, *cupric sulphate* a green, *lead acetate*, neutral or basic, a white precipitate;

the lead precipitate is soluble in acetic acid as well as in excess of the precipitant. *Mercurous salts* form white precipitates, becoming grey at the boiling heat; *mercuric chloride* yields on boiling a precipitate of calomel.

Hydrophthalic acid is bibasic, forming acid and neutral salts, the former crystallising the more easily. The easily soluble *sodium salt* forms spherical groups of shining laminæ. The *neutral barium salt*, $C^8H^6O^4Ba$, separates on evaporation in nacreous crusts, easily soluble in warm, less soluble in cold water. The *acid barium salt*, $(C^8H^7O^4)^2Ba + H^2O$, forms stellate groups of crystals, easily soluble in water, sparingly in alcohol, becoming anhydrous at 120°–130°. The *neutral calcium salt*, $C^8H^6O^4Ca$, and the acid salt, $(C^8H^7O^4)^2Ca$, are slightly soluble in water, and crystallise indistinctly. The *lead salt*, $C^8H^6O^4Pb$, is a crystalline powder nearly insoluble in water, easily soluble in dilute acetic acid. The *silver salt* is a white precipitate, moderately soluble in water, becoming black on boiling, and depositing silver, especially in presence of ammonia.

Decompositions.—1. Hydrophthalic acid heated above 200° gives off water and melts to a yellow liquid, which decomposes partially at a higher temperature, yielding a yellow oily solidifying distillate, from which by recrystallisation from alcohol, phthalic anhydride, $C^8H^4O^3$, is obtained.—2. Heated with *soda-lime* it is resolved into benzene, hydrogen, and carbon dioxide:

$$C^6H^6(CO^2H)^2 = C^6H^6 + 2CO^2 + H^2.$$

3. With *phosphorus pentachloride*, it yields benzoyl chloride, carbon monoxide, hydrochloric acid, and phosphorus oxychloride:

$$C^6H^6(CO^2H)^2 + 2PCl^5 = C^6H^5(COCl) + CO + 3HCl + 2POCl^3.$$

4. Heated with strong *sulphuric acid*, it yields phthalic acid, benzoic acid, and carbon monoxide:

$$C^6H^6(CO^2H)^2 + SO^4H^2 = C^6H^4(CO^2H)^2 + 2H^2O + SO^2$$

and

$$C^6H^6(CO^2H)^2 = C^6H^5(CO^2H) + CO + H^2O.$$

5. A solution of hydrophthalic acid heated with a slight excess of *bromine* yields benzoic acid, hydrobromic acid, and carbon dioxide (with a small quantity of phthalic acid):

$$C^6H^6(CO^2H)^2 + Br^2 = C^6H^5(CO^2H) + 2HBr + CO^2.$$

6. Fused with *potassium hydrate*, it yields benzoic acid, together with hydrogen and carbon dioxide:

$$C^6H^6(CO^2H)^2 = C^6H^5(CO^2H) + H^2 + CO^2.$$

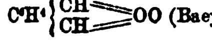
7. By oxidation with dilute *nitric acid* or with *chromic acid*, it is converted into benzoic and phthalic acids.—8. The alcoholic solution of hydrophthalic acid treated with *hydrochloric acid gas*, yields, not hydrophthalate, but benzoate of ethyl, perhaps together with formate, according to the equation:

$$C^6H^6(CO^2)H^2 + 2C^2H^6O = C^6H^5(CO^2C^2H^5) = HCO^2C^2H^5 + 2H^2O.$$

Hydroterephthalic acid, $C^8H^8O^4$, is formed by treating terephthalic acid in moderately soluble concentrated alkaline solution with sodium-amalgam for several days, and separates, on neutralising with hydrochloric acid, as a white flocculent precipitate, quite insoluble in water, and reducing ammoniacal silver solution at the boiling heat (R. Mohs, *Zeitschr. f. Chem.* [2] iii. 68).

PHTHALIC ALDEHYDE, $C^8H^6O^2$, is formed by the action of zinc and hydrochloric acid on phthalic chloride. When dissolved out by ether and purified, it forms a white slightly aromatic substance, melting at 65°, easily soluble in alcohol and ether, slightly soluble in cold, more abundantly in hot water, and crystallising therefrom in small rhombic tables. The warm aqueous solution solidifies with sodium bisulphite to a mass of silky needles (Kolbe a. Wischin, *Chem. Soc. J.* [2] iv. 339).

Phthalic aldehyde is also the chief product formed by the action of magnesium on a solution of phthalic chloride in glacial acetic acid. It volatilises at 180° with vapour of water, and exhibits remarkable stability, perhaps arising from the union of each of its oxygen-atoms with two atoms of carbon, as represented by the formula



$$C^6H^4\left\{\begin{matrix}CH\\CH\end{matrix}\right.\!\!>OO$$

(Baeyer, *Zeitschr. f. Chem.* [2] v. 399).

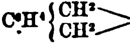
PHTHALIC ANHYDRIDE, $C^8H^4O^3$, is produced in the decomposition of hydrophthalic acid by heat (p. 943). It melts at 128° (Lossen; Carius; Hermann); at 129° (Graebe a. Born); the melting point 105° given by Laurent (iv. 631) is much too low; boils at 276° (Lossen).

PHTHALIC CHLORIDE, $C^8H^4O^2Cl^2$, produced by the action of phosphorus pentachloride on phthalic acid or anhydride (iv. 633), boils at 270° (H. Müller): at 268°, and solidifies at 0° (Wischin, *Ann. Ch. Pharm.* cxliii. 259; *Jahresb.* 1867, p. 722). It is but slowly decomposed by water or by aqueous sodium carbonate. Zinc-ethyl converts it (dissolved in benzol) into phenylene-diethyl ketone (Wischin):

$$C^6H^4(COCl)^2 + Zn(C^2H^5)^2 = ZnCl^2 + C^6H^4(C^2H^5)^2C^2O^2.$$

Phthalic chloride dissolves in glacial acetic acid, and on heating the solution, hydrochloric acid is given off, and a crystalline body is formed, which is decomposed by water, and doubtless consists of acetophthalic anhydride:

$$C^6H^4(COCl)^2 + 2C^2H^3O(OH) = 2HCl + C^6H^4(CO.O.C^2H^3O)^2.$$

When magnesium is added to a solution of phthalic chloride in about 20 pts. glacial acetic acid, and the resulting liquid is neutralised and agitated with ether, phthalic aldehyde is obtained as principal product, together with a small quantity of oil volatilising easily with vapour of water, and having approximately the composition of the anhydride of phthalic alcohol,  $C^6H^4\left\{\begin{array}{l}CH^2\\CH^2\end{array}\right.\!\!>O$ (Baeyer, *Zeitschr. f. Chem.* [2] v. 399).

PHTHALOSULPHURIC ACID, $C^8H^6SO^7$, analogous to succinyl-sulphuric acid, is formed, according to O. Loew (*Ann. Ch. Pharm.* cxliii. 257), by heating phthalic acid to 100°–105° for some time with excess of sulphuric anhydride, and leaving the product exposed to moist air. It solidifies to a crystalline mass when evaporated in a vacuum over sulphuric acid, but its salts are uncrystallisable. Their aqueous solutions, as well as that of the acid, are decomposed by boiling or by gradual evaporation, with liberation of sulphuric acid. The barium salt contains $C^8H^4SO^7Ba$.

PHYLLESCITANNIN. $C^{26}H^{24}O^{13}.H^2O$.—A tannin existing in the small leaflets of the horse-chestnut, as long as they remain enclosed in the buds (Rochleder, *Jahresb.* 1866, p. 694).

PHYLLOCYANIC ACID and **PHYLLOXANTHIN** (iv. 633).—According to later experiments by Frémy (*Bull. Soc. Chim.* [2] v. 464; *Jahresb.* 1865, p. 585), it appears that pure chlorophyll is resolved into these two bodies by boiling with baryta-water, both separating in the insoluble form, the former as barium salt. On treating the precipitate with alcohol, the phylloxanthin dissolves, whilst the insoluble barium phyllocyanate decomposed by sulphuric acid yields phyllocyanic acid soluble in alcohol and ether.

PHYSOSTIGMINE. Further details respecting the preparation and properties of this base, the poisonous principle of the Calabar bean, have been given by Hesse (*Ann. Ch. Pharm.* cxli. 82; *Jahresb.* 1867, p. 528). Its composition is $C^{15}H^{21}N^3O^2$. Potassio-mercuric iodide throws down from its salts a white easily fusible precipitate of the double salt, $C^{15}H^{21}N^3O^2.HI.HgI^2$. Physostigmine throws down ferric oxide from a neutral solution of ferric chloride; forms a kermes-coloured precipitate with a solution of iodine in potassium iodide; and is precipitated by tannic acid, mercuric chloride, and auric chloride, but not by platinic chloride.

PICOLINE, C^6H^7N, is produced by the distillation of acrolein-ammonia. This reaction explains the formation of picoline in the dry distillation of animal substances. The fats yield acrolein, and this compound, in contact with ammonia at a high temperature, yields first acrolein-ammonia, C^6H^9NO, and then picoline:

$$2C^3H^4O + NH^3 = H^2O + C^6H^9NO$$

and

$$C^6H^9NO = H^2O + C^6H^7N$$

(Baeyer, *Zeitschr. f. Chem.* [2] v. 570).

PICRAMIC ACID.
PICRAMINE. } See AMIDOPHENOLS (p. 915).

PICRIC ACID. See TRINITROPHENOL (p. 911).

PICROERYTHRIN. $C^{12}H^{16}O^7$ (iv. 641).—This body is obtained with peculiar facility in the pure state by boiling erythrin for several hours with amyl alcohol:

$$\underset{\text{Erythrin.}}{C^{20}H^{22}O^{10}} + \underset{\substack{\text{Amyl}\\\text{alcohol.}}}{C^5H^{12}O} = \underset{\text{Amyl orsellinate.}}{C^8H^7O^4.C^5H^{11}} + \underset{\text{Picroerythrin.}}{C^{12}H^{16}O^7}$$

When the reaction is complete, part of the alcohol is distilled off, and the remaining liquid is heated over the water-bath, whereupon amyl orsellinate separates as an oily layer, while the picroerythrin crystallises from the filtered liquid at about 40° in white silky prisms consisting of $C^{12}H^{16}O^7.3H^2O$ (Hesse, *Jahresb.* 1866, p. 659).

PIMARIC ACID. Maly (*Ann. Ch. Pharm.* cxxix. 94; cxxxii. 253; *Zeitschr. f. Chem.* [2] v. 304) regards this acid as identical with his abietic acid, $C^{44}H^{64}O^5$; but Duvernoy (*Ann. Ch. Pharm.* cxlviii. 143; *Zeitschr.* [2] v. 303), working under Strecker's direction, has confirmed the results obtained by Laurent and by Siewert (iv. 615), according to which pimaric acid is isomeric with sylvic acid, and has the composition $C^{20}H^{30}O^2$.

Pimaric acid prepared from French galipot by washing with cold dilute alcohol till that liquid no longer becomes yellow, and crystallising from boiling alcohol, forms hard granular crusts, appearing under the microscope to be made up of well-defined rectangular crystals; it is insoluble in water, slightly soluble in cold, freely in hot alcohol and ether. It melts at 149°, and boils at a temperature above 320° (Duvernoy); according to Laurent, it melts at 125°, according to Sievert at 155°.

Sodium pimarate, $C^{20}H^{29}O^2Na + 4H^2O$, separates from a solution of the acid in excess of very dilute soda-ley, in shining crystals, and is obtained by recrystallisation from alcohol in nacreous laminæ. It is nearly insoluble in cold water, easily soluble in hot water, also in alcohol and ether; a large quantity of water decomposes it into an acid salt and free alkali. It gives off its water at 100°, and is not decomposed at 140°. An *acid potassium salt*, $C^{20}H^{29}O^2K.2C^{20}H^{30}O^2$, separates in the crystalline form when pimaric acid is added to hot alcoholic potash till the alkaline reaction is nearly neutralised; it dissolves sparingly in water, easily in alcohol, and melts at 121°. The neutral potassium salt was obtained in very small quantity only. The *acid ammonium salt*, $C^{20}H^{29}O^2(NH^4).C^{20}H^{30}O^2$, separates from a solution of the acid in aqueous ammonia, in long silky needles, soluble in water, but decomposed by a large quantity of water. The *magnesium*, *calcium*, *barium*, *strontium*, and *lead salts* may be easily prepared from the sodium salt and purified by alcohol and ether. The *silver salt*, $C^{20}H^{29}O^2Ag$, quickly turns red on exposure to light. Laurent a. Sievert describe all these salts as uncrystalline; Laurent indeed indicates the uncrystallisability of the lead salt as affording a distinction between pimaric and sylvic acids; Duvernoy, however, obtained the lead salt crystallised from ether.

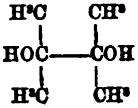
When hydrochloric acid gas is passed into an alcoholic solution of pimaric acid, a modified pimaric acid is deposited, as a crystalline precipitate, which forms with ammonia, not a crystalline, but a gelatinous salt. The free acid melts at 143°, and crystallises from alcohol in microscopic truncated triangular plates. This modification, as well as the former, turns the plane of polarisation to the left.

Pimaric acid yields, by distillation, a yellow, transparent, brittle, acid resin, the alcoholic solution of which does not deposit crystals. The ammonium salt of this acid is gelatinous when first prepared, but changes in a few days into needle-shaped crystals. The free acid melts at 129°, and is not therefore unaltered pimaric acid, as stated by Sievert. Sylvic acid prepared from colophony melts at 129°, and likewise yields a gelatinous ammonium salt (Duvernoy; see also Strecker, *Ann. Ch. Pharm.* cl. 131).

PIMELIC ACID, $C^7H^{12}O^4$, is formed, together with other products, by fusing camphoric acid with potash (Hlasiwetz a. Grabowski). See CAMPHORIC ACID (p. 389).

PINACONE. $C^6H^{14}O^2$.—The following additional observations on this body have been made by Friedel (*Zeitschr. f. Chem.* [2] v. 485). Pinacone is not susceptible, as supposed by Linnemann (iv. 648), of two modifications, one liquid and the other solid, the supposed liquid modification being merely in a state of surfusion, like water cooled under certain circumstances below 0°. In fact, pinacone, when distilled in an oil-bath, may remain fluid for a long time after cooling, but rapidly crystallises, with rise of temperature, on rubbing the sides of the vessel with a glass rod.

Pinacone exhibits the chemical relations of a glycol. On treating it in the cold with hydrochloric acid gas, a chlorinated product is obtained which is decomposed by distillation, and when treated with potash yields pinacolin, $C^6H^{12}O$ (iv. 647). This latter product is likewise formed by treating pinacone with glacial acetic acid. Pinacone is not converted into pinacolin by merely heating it strongly in a sealed tube. Phosphorus pentachloride acts strongly on pinacone, converting it, with evolution of hydrochloric acid, into a chloride, which appears to have the composition of hexylene chloride, $C^6H^{12}Cl^2$, and boils, apparently with decomposition, at about 160°. Treated with sodium this chloride yields an oily liquid boiling between 60° and 70°, and apparently consisting of hexylene. Friedel represents pinacone by the formula



$$\begin{array}{cc} H^3C & CH^3 \\ | & | \\ HOC & \!\!-\!\!-\!\!-\; COH \\ | & | \\ H^3C & CH^3 \end{array}$$

that is to say, as tetramethylated ethyl-glycol, and the hexylene obtained from it as tetramethylated ethylene.

PIPERIC ACID. $C^{12}H^{10}O^4 = C^{11}H^9O^2.CO^2H$ (Fittig a. Mielck, *Ann. Ch. Pharm.* clii. 25; *Zeitschr. f. Chem.* [2] v. 326).—This acid, prepared according to the method of v. Babo a. Keller (iv. 653) by heating piperine with alcoholic potash, and purified by separation from its potassium salt and recrystallisation, melts in the first instance at 216°–217°; but after being once fused, it melts constantly at 212°–213°, not at 150° as stated by v. Babo a. Keller. When heated a few degrees above its melting point, it sublimes with partial decomposition in slender needles. It may be heated with pure *water* to 230° for days without sensible decomposition, but between 235° and 245° it decomposes completely into carbon dioxide and a mixture of non-acid resinous bodies. Very weak *hydrochloric acid* appears to produce the same decomposition even below 160°, strong hydrochloric acid at 100°. Piperic acid heated with *quick lime* decomposes almost completely into water, carbon dioxide, and free carbon, with only a trace of an oil very much like phenol.

Potassium piperate heated with *ethyl iodide*, potash, and alcohol, yields only ethylic piperate, not a trace of ethylic ethyl-piperate. Piperic acid is not decomposed by *acetyl chloride*, even when heated therewith in sealed tubes, and when heated with *hydriodic acid*, it yields only a trace of a volatile iodine compound: hence it appears that the two oxygen-atoms in piperic acid not included in the carboxyl group are not present as HO, or as CH^3O, C^2H^5O, &c.

Piperic acid is oxidised by *chromic acid* mixture, even at ordinary temperatures, quickly and completely at a gentle heat, the only products being water and carbon dioxide. Mixed in neutral solution with aqueous *potassium permanganate*, it instantly reduces that compound, and is oxidised to piperonal, $C^8H^6O^3$ (p. 947), together with oxalic acid, carbon dioxide, and water:

$$C^{12}H^{10}O^4 + O^8 = C^8H^6O^3 + C^2H^2O^4 + 2CO^2 + H^2O.$$

A small quantity of the piperonal is further oxidised to piperonylic acid. Dilute *nitric acid* acts very strongly on piperic acid, producing a red, non-acid, amorphous body, sparingly soluble in the ordinary solvents, and completely dissolved by prolonged boiling with nitric acid, yielding a large quantity of oxalic acid. The solution filtered from the red substance contains piperonal or a nitro-derivative of it, which crystallises well and melts at 138°–139°.

When piperic acid is triturated with a small quantity of water, and with *bromine* gradually added to it, the bromine is slowly taken up; and on washing the product with water and dissolving it in hot alcohol, unaltered piperic acid crystallises out, and the mother-liquor leaves on evaporation a non-acid resinous body, which when distilled with aqueous sodium carbonate, yields a colourless distillate of monobromopiperonal, $C^8H^5BrO^3$, which crystallises in the condensing-tube in needles. This body does not exist ready-formed in the resin, but is produced from it by the action of the sodium carbonate, for the resin does not yield it by distillation with pure water. The nature of the constituent of the resin from which the bromopiperonal is formed has not been exactly made out; but it appears to be a body having the composition $C^9H^9Br^3O^6$, which may be obtained in the separate state by agitating 1 mol. piperic acid suspended in water with an ethereal solution of 4 mol. bromine, whereupon the piperic acid disappears, and a heavy red ethereal liquid gradually settles to the bottom; on agitating the whole with solution of sodium carbonate, the colour disappears, the ether rises to the top, and numerous small colourless nacreous laminæ separate, the composition of which may be represented by the formula $C^9H^9Br^3O^6$. From this compound the bromopiperonal may be found according to the equation:

$$C^9H^9Br^3O^6 = C^8H^5BrO^3 + CO^2 + 2HBr + H^2O.$$

Another substance remains dissolved in the ether, and may be obtained, by evaporation and repeated crystallisation from alcohol, in colourless prisms whose composition may be represented empirically by either of the formulæ, $C^{12}H^{8}Br^{2}O^{4}$ or $C^{12}H^{10}Br^{2}O^{4}$. This body gently heated with strong potash-ley yields piperonal.

Hydropiperic acid, $C^{12}H^{12}O^{4}$, reacts with oxidising agents and with bromine very much like piperic acid. Treated in neutral solution with potassium permanganate, it likewise yields piperonal; but the reaction is not so definite as with piperic acid; the piperonal which distils over is not quite pure; and the residue of the distillation yields with hydrochloric acid a black viscid resinous precipitate.

PIPERIDINE. $C^{5}H^{11}N$ (Wertheim, *Ann. Ch. Pharm.* cxxvii. 75).—This base may be prepared directly from pepper by distilling the alcoholic extract with excess of caustic potash, ultimately with addition of a little water. The nearly colourless alkaline distillate containing a small quantity of volatile oil, together with piperidine and ammonia, is saturated with sulphuric or hydrochloric acid, and evaporated to dryness; the residue is exhausted with absolute alcohol; the solution again evaporated; and the admixed pepper-oil is separated by solution in a small quantity of water, filtering through a wet filter, and repeated evaporation over the water-bath. The concentrated aqueous solution is then decomposed with caustic potash, and the oily layer of piperidine thereby separated is rectified. 28 kilogr. of pepper (white and black in equal parts) thus treated yield 350 grm. pure piperidine.

The crystalline forms of several piperidine salts have been determined by Zepharovich (*Wien. Akad. Ber.* lii. [1] 241; *Jahresb.* 1866, p. 479).

Nitrosopiperidine. $C^{5}H^{10}N^{2}O = N\left\{\begin{matrix}(C^{5}H^{10})'' \\ NO\end{matrix}\right.$ (Wertheim, *loc. cit.*).—When piperidine is slowly saturated with nitrous acid, a dark emerald-green liquid is formed, which, after the excess of nitrous acid has been removed by slowly passing carbon dioxide through it at 30°–40°, changes to a wine-yellow oil having a pungently acid but aromatic odour; and on mixing this oil, first with an equal volume of water, then by drops and in a well-cooled vessel with strong potash-ley, a yellowish-red oil separates, which, by agitation with dilute hydrochloric or glacial phosphoric acid, drying over calcium chloride, and rectification at 160°, yields pure nitrosopiperidine. This compound is likewise formed, according to Bunge (*Zeitschr. f. Chem.* [2] v. 649), together with water, by distilling piperidine nitrite.

Nitrosopiperidine is a pale, wine-yellow, neutral liquid, having an unpleasant aromatic odour and burning aromatic taste. Sp. gr. 1·0659 at 15·5°. It volatilises without alteration at 160°–180°, and boils at 240° with partial decomposition. Vapour-density 4·04 (calc. 3·94). It dissolves with moderate facility in water, much more easily in acids, especially in concentrated acids, and is precipitated therefrom by water, also in aqueous solution by common salt.

Nitrosopiperidine is reconverted by nascent hydrogen (zinc and hydrochloric acid) into piperidine, with simultaneous formation of ammonia and water:

$$C^{5}H^{10}(NO)N + 3H^{2} = C^{5}H^{11}N = NH^{3} + H^{2}O.$$

Heated to 100° in hydrochloric acid gas, it yields piperidine hydrochloride and chloronitrous acid:

$$C^{5}H^{10}N^{2}O + 2HCl = C^{5}H^{11}N.HCl + NOCl.$$

At ordinary temperatures hydrochloric acid gas is absorbed by nitrosopiperidine, forming a colourless mass probably consisting of $C^{5}H^{10}N^{2}O.HCl$. On continuing the passage of the gas, the crystalline compound melts to a syrupy liquid, the increase in weight of which corresponds to the formula $C^{5}H^{10}N^{2}O.2HCl$. Both these salts are completely decomposed by water, with separation of nitrosopiperidine. The platinochloride has not been obtained (Wertheim).

PIPERINE. $C^{17}H^{19}NO^{3}$.—A warm solution of this base in alcohol containing hydrochloric acid, mixed with the requisite quantity of a solution of iodine in potassium iodide, deposits on cooling steel-blue prisms of the compound $2C^{17}H^{19}NO^{3}.HI^{3}$ (Jörgensen, *Zeitschr. f. Chem.* [2] v. 675).

PIPERONAL. $C^{8}H^{6}O^{3} = C^{7}H^{5}O^{2}.CHO = C^{6}H^{3}—O—CO—COH$ (Fittig a. Mielck, *Ann. Ch. Pharm.* clii. 35; *Zeitschr. f. Chem.* [2] v. 327; Remsen a. Fittig, *Zeitschr.* [2] vi. 97).—Produced by oxidation of piperic acid in neutral solution with potassium permanganate (p. 946). When an aqueous solution of potassium piperate is mixed with permanganate, each drop of the latter is almost instantly decolorised, and brown manganic hydrate is separated. The solution acquires a very pleasant odour, like that of coumarin, and yields piperonal by distillation.

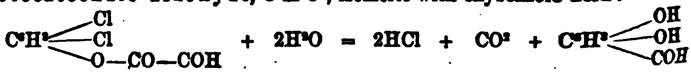
Piperonal crystallises from water in colourless, transparent, highly lustrous prisms, an inch long and a line broad. It is sparingly soluble in cold water, more easily in hot water, easily in cold alcohol, and in all proportions of boiling alcohol and of ether. It has a very agreeable odour, much like that of coumarin, melts exa[illegible] 37°, and boils without decomposition at 263°. *It has decidedly the characters* [illegible] aldehyde, forming with *acid sodium sulphite* a compound like that of benzoic [illegible] crystallising in laminæ slightly soluble in water and in alcohol; with [illegible] *ammonia*, a basic compound very slightly soluble in water. By further oxid[illegible] by heating with alcoholic potash it is converted into an acid containing an [illegible] atom of oxygen. It is not altered by aqueous alkalis, but passes over almost un[illegible] posed even when distilled with moderately concentrated potash- or soda-ley. [illegible] it is not a hydroxyl-phenol. Heated with water and *sodium-amalgam*, it [illegible] piperonyl alcohol, $C^8H^8O^3$, and two isomeric bodies, hydropiperoïn [illegible] iso-hydropiperoïn, $C^{16}H^{14}O^6$, analogous to hydrobenzoïn.

Bromopiperonal, $C^8H^5BrO^3$, produced, as above described (p. 946), by [illegible] piperic acid with bromine, and distilling the product with sodium carb[illegible] insoluble in cold, somewhat soluble in boiling water, easily soluble in hot, [illegible] in cold alcohol, and crystallises from alcohol in long, flexible, shining, [illegible] needles; melts at 129°, volatilises perceptibly at 70°, and so easily with [illegible] water that narrow condensing tubes are very soon stopped up by it. Cold [illegible] nitric acid converts it into a well-crystallised nitro-compound. With sodium-am[illegible] it yields piperonal and its products of reduction.

Chlorinated Derivatives of Piperonal.—1 mol. piperonal and 1 mol. [illegible] phorus pentachloride mixed together at ordinary temperatures produce piper[illegible] chloride, $C^7H^5O^2.CHCl^2$, according to the equation:

$$C^7H^5O^2.CHO + PCl^5 = PCl^3O + C^7H^5O^2.CHCl^2.$$

This compound is liquid, boils at 230°–240°, but decomposes for the most part [illegible] distillation, and is slowly reconverted by water at ordinary temperatures [illegible] piperonal. When 1 mol. piperonal is heated with 3 mol. PCl^5, hydrochloric [illegible] evolved, phosphorus oxychloride distils over, and there remains a colourless or [illegible] yellow liquid, consisting of dichloropiperonal chloride, $C^7H^3Cl^2O.CH$[illegible] boils at about 280°, and thickens but does not solidify at low temperatures. In [illegible] tact with water or with moist air it is quickly resolved into hydrochloric acid [illegible] dichloropiperonal, $C^8H^4Cl^2O^3 = C^7H^3Cl^2O^2.COH$ or $C^6H^2Cl^2—O—CO—$[illegible] a solid body, insoluble in cold water, easily soluble in alcohol and in toluene, [illegible] crystallising from the latter in colourless needles. This last compound *boiled* [illegible] water, or heated to 100° with water in sealed tubes, gives up the *whole* of its chlor[illegible] as hydrochloric acid, and is converted, with elimination of carbon dioxide, [illegible] protocatechuic aldehyde, $C^7H^6O^3$, isomeric with oxybenzoic acid:



$$C^6H^2\begin{cases}Cl\\Cl\\O—CO—COH\end{cases} + 2H^2O = 2HCl + CO^2 + C^6H^3\begin{cases}OH\\OH\\COH\end{cases}$$

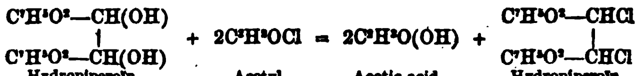
Dichloropiperonal. Protocatechuic aldehyde.

Nitropiperonal, $C^8H^5(NO^2)O^3$, is formed when piperonal, piperonyl alcoh[illegible] hydropiperoïn, or isohydropiperoïn, is warmed with nitric acid of sp. gr. 1·39. On pouring the resulting solution into water, the nitro-compound separates as a lig[illegible] yellow crystalline mass. It is nearly insoluble in cold water, but dissolves easily in hot water and in alcohol, and crystallises from water in long colourless needles which quickly become golden-yellow on exposure to the air. It melts at 95·5° (Remsen & Fittig).

Hydropiperoïn. $C^{16}H^{14}O^6$.—This compound, formed by the action of nascent hydrogen on piperonal, is nearly insoluble in water even at the boiling heat, also in cold alcohol, sparingly soluble in hot alcohol, and separates therefrom on *cooling* in stellate groups of hard pointed crystals melting at 202°.

Isohydropiperoïn, $C^{16}H^{14}O^6$, is also nearly insoluble in cold water, but may be recrystallised from boiling water. It dissolves easily in alcohol, and may therefore be readily separated by alcohol from hydropiperoïn. It crystallises in felted groups of long soft needles which melt at first at 138°, but after being once liquefied, melt again at 135°.

Acetyl chloride converts hydropiperoïn slowly, and isohydropiperoïn more quickly, into hydropiperoïn chloride, $C^{16}H^{12}O^4Cl^2$, as represented by the following equation:



$$\begin{matrix}C^7H^5O^2—CH(OH)\\|\\C^7H^5O^2—CH(OH)\end{matrix} + 2C^2H^3OCl = 2C^2H^3O(OH) + \begin{matrix}C^7H^5O^2—CHCl\\|\\C^7H^5O^2—CHCl\end{matrix}$$

Hydropiperoïn. Acetyl chloride. Acetic acid. Hydropiperoïn chloride.

This chloride is nearly insoluble in water and alcohol at ordinary temperatures. By prolonged boiling with water it is decomposed, with formation of hydrochloric acid. It becomes slightly yellow at 150°, melts at 198°, decomposes immediately after fusion, with evolution of gas, and is converted into a viscid brownish-yellow mass which does not resolidify on cooling (Remsen a. Fittig). See further, *Ann. Ch. Pharm.* clix. 129; *Chem. Soc. J.* [2] ix. 934.

PIPERONYL ALCOHOL, $C^8H^8O^3$, also a product of the action of sodium-amalgam on piperonal, forms colourless crystals melting at 51°. It is very sparingly soluble in water, separates therefrom as a liquid, and remains liquid for a long time in contact with water. In alcohol it dissolves in almost all proportions. It is not volatile without decomposition. With acetyl chloride it gives off hydrochloric acid, and forms a liquid acetic ether (Remsen a. Fittig).

PIPERONYLIC ACID, $C^8H^6O^4$, is formed in small quantity, as a secondary product, in the preparation of piperonal, and may be separated from the residue of the distillation by hydrochloric acid. From pure piperonal it is easily obtained by adding potassium permanganate to the aqueous solution till the odour of the piperonal disappears, then filtering, evaporating, and precipitating with hydrochloric acid. It may also be prepared, though less pure, by boiling piperonal with alcoholic potash. The acid obtained in either way may be purified by recrystallisation from alcohol and sublimation. It is nearly insoluble in cold water, sparingly soluble in boiling water, alcohol, and ether, more easily in boiling alcohol. From boiling water it crystallises in large, thick, colourless, spicular crystals, apparently monoclinic prisms with oblique end-faces. When perfectly purified by repeated sublimation, it melts exactly and without the slightest coloration at 227·5° to 228·5°. It sublimes below its melting point, and, if quite pure, without decomposition.

Piperonylic acid is monobasic, and must therefore differ in constitution from phthalic acid, with which it is isomeric. The *potassium salt*, $C^8H^5O^4K$, crystallises from hot alcohol in small, hard, colourless prisms; from water in small, hard, inconspicuous needles. It is easily soluble in water, moderately in boiling alcohol, sparingly in cold alcohol. The *silver salt*, $C^8H^5O^4Ag$, is obtained as a granular crystalline precipitate, and crystallises from hot water in long, narrow, colourless laminæ permanent in the air. The *barium salt*, $(C^8H^5O^4)^2Ba + H^2O$, is easily soluble in hot water, and crystallises therefrom in hard shining prisms. The *calcium salt*, $(C^8H^5O^4)^2Ca + 3H^2O$, forms tufts of colourless silky needles or laminæ, moderately soluble in cold, easily in hot water. The *zinc salt* forms large colourless pointed crystals sparingly soluble in cold water.

The solution of the potassium salt forms a cinnamon-coloured precipitate with ferric chloride, white with mercuric chloride and with lead nitrate. With cupric solutions in the cold it forms a bright green precipitate which, when heated in the liquid, quickly becomes light blue, almost colourless.

Piperonylic acid reacts almost exactly like piperic acid with chromic acid solution, and when distilled with excess of lime. It is also easily oxidised by dilute nitric acid, with formation of oxalic acid and carbon dioxide. By sodium-amalgam it is very slowly converted into an acid, which dissolves very easily in hot water and in ether, and exhibits the general characters of an aromatic hydroxylic acid (Fittig a. Mielch, *loc. cit.*).

When piperonylic acid is heated with dilute hydrochloric acid in sealed tubes to 160°–200°, a black mass separates, consisting almost wholly of free carbon, and the nearly colourless solution yields on evaporation protocatechuic acid or pyrocatechin, according to the temperature to which the materials have been heated. At 160°–170°, the product is almost wholly protocatechuic acid, but at 190°–200° pyrocatechin is formed, with elimination of carbon dioxide:

$$\underset{\substack{\text{Piperonylic}\\\text{acid.}}}{C^8H^6O^4} = \underset{\substack{\text{Protocate-}\\\text{chuic acid.}}}{C^7H^6O^4} + C; \text{ and } \underset{\substack{\text{Piperonylic}\\\text{acid.}}}{C^8H^6O^4} = \underset{\text{Pyrocatechin.}}{C^6H^6O^2} + C + CO^2.$$

The quantities of these bodies obtained are, however, much below the theoretical quantities (Remsen a. Fittig, *Zeitschr. f. Chem.* [2] vi. 101) See further, *Ann. Ch. Pharm.* clix. 129; *Chem. Soc. J.* [2] ix. 936.

PLATINUM. A method of separating platinum from the allied metals, founded on its behaviour with caustic soda, is given by W. von Schneider (*Ann. Ch. Pharm. Suppl.* v. 261). Platinic chloride in aqueous solution is scarcely, if at all, reduced to platinous chloride by excess of sodium hydrate, even after prolonged boiling, whereas the higher chlorides of the other platinum metals, when similarly treated, are more or less converted (with formation of sodium chloride and hypochlorite) into lower chlorides not precipitable by sal-ammoniac. The separation may therefore be effected as follows. The platinum ore having been exhausted with nitromuriatic acid, and nitric acid removed by evaporation, the solution is mixed with a very large excess of soda-ley free from potash, and boiled till a small portion of the platinum tetrachloride is reduced to dichloride; a little alcohol is added to decompose sodium hypochlorite; the precipitate is redissolved in hydrochloric acid; and the solution, filtered if necessary, is mixed with a hot-saturated solution of sal-ammoniac, whereby, if the prescribed conditions have been accurately observed, the platinum alone is precipitated as yellow ammonium platinochloride. If, on the contrary, the excess of soda-ley added has not been sufficient, the precipitated platinochloride contains some of the other platinum metals, which remain behind when the platinum-sponge prepared therefrom is dissolved. The metals remaining in solution are precipitated at the boiling heat by a strip of copper-plate; the precipitated metallic powder is washed, the palladium dissolved out of it by nitric acid; and the residue, which still contains platinum, is added to the next preparation.

Döbereiner's method of purifying platinum solutions by treatment with calcium hydrate is the same in principle as that just described, the higher chlorides of all the metals of the group except platinum being thereby also reduced to lower chlorides; but it does not effect complete separation, as Schneider has shown by analysis of Russian platinum coins and platinum-sponge which had been purified by Döbereiner's method.

Platinum and iridium may be separated by the different solubilities of their sulphites. The mixed oxides of the two metals are suspended in a solution of potassium carbonate or sulphite; the liquid is saturated with sulphurous acid; and the solution (containing all the platinum as platinous sulphite, and part of the iridium as potassio-iridic sulphite) is boiled with the precipitate (iridic sulphite), the water being renewed as it evaporates, to expel the free sulphurous acid. The whole of the iridium is thereby separated; and the filtrate, evaporated, ignited, and washed, yields pure metallic platinum (Birnbaum, *Ann. Ch. Pharm.* cxxxix. 164).

Respecting the absorption or occlusion of hydrogen by platinum, see GASES, ABSORPTION OF (p. 634).

Platinisation of Metals.—A convenient liquid for this purpose is prepared by adding sodium carbonate to a solution of platinic chloride as long as carbon dioxide is thereby evolved, then a small quantity of starch-sugar, and finally common salt, till the precipitated metal exhibits a pure white platinum colour. Small objects may be platinised by mere contact action (Böttger, *J. pr. Chem.* [2] iv. 524).

Bromides (Topsöe, *Jahresb.* 1868, p. 274).—*Acid Platinic Bromide* or *Hydroplatinic Bromide*, $PtBr^4.2HBr + 9H^2O$, is obtained, by dissolving platinum-sponge in a mixture of nitric acid and excess of hydrobromic acid, and evaporating the solution over quick lime, in transparent, crimson, very deliquescent prisms, apparently belonging to a clinometric system. They melt at 100°, giving off water, hydrobromic acid, and bromine, and ultimately leave a solid mass of platinous bromide and undecomposed acid platinic bromide; neutral platinic bromide cannot be obtained in this way. To obtain platinous bromide, $PtBr^2$, acid platinic bromide is heated to 200° till it is converted into a solid yellow mass; this, when lixiviated with water, yields the dibromide as a greenish-brown powder, insoluble in water, moderately soluble in hydrobromic acid and potassium bromide. It withstands a temperature of 240° for a short time, but is partially decomposed by prolonged heating to 200°.

Bromonitrite of Platinic Bromide, $PtBr^4.2NOBr$, is formed when platinum is treated with a mixture of hydrobromic acid and excess of nitric acid, and separates as a dark brown metallically shining powder, composed of microscopic cubes, deliquescing in the air with evolution of bromonitrous acid, and decomposed by water with evolution of nitrogen tetroxide.

Platinobromides.—*Ammonium platinobromide*, $2NH^4Br.PtBr^4$, is obtained by precipitation as a crystalline orange-coloured powder, the solution of which in 200 pts. of water deposits the salt by spontaneous evaporation in large, shining, crimson cubo-octohedrons. The *sodium salt*, $2NaBr.PtBr^4 + 6H^2O$, crystallises in irregularly developed, mostly tabular, triclinic prisms, isomorphous with the corresponding chlorine-compound. The following platinobromides have been prepared by saturating acid platinic bromide with the corresponding carbonates. The *barium* and *strontium salts*, $M''Br^2.PtBr^4 + 10H^2O$, apparently isomorphous, form crimson, laminar, somewhat deliquescent crystals. The *lead salt*, $PbBr^2.PtBr^4$, forms shining red-brown granules easily soluble in a small quantity of water, partially decomposed by a larger quantity. The *cupric salt*, $CuBr^2.PtBr^4 + 8H^2O$, forms large tabular, apparently rhombic, deliquescent crystals. The *nickel salt*, $NiBr^2.PtBr^4 + 6H^2O$, crystallises in brownish-green combinations of a rhombohedron with a prism of the second order (axes $a : c$ = 1 : 0·5136; angle of terminal edges = 127° 34′), and is isomorphous with the corresponding double chloride. The platinobromides of *magnesium*, *manganese*, *zinc*, and *cobalt* have the general formula $M''Br^2.PtBr^4 + 12H^2O$; they are very soluble, but crystallise easily in irregularly developed rhombohedral combinations containing the same amount of water as the corresponding platinochlorides:

	Length of principal axis *c* of the rhombohedron ($a = 1$)	Terminal angle of rhombohedron
$MgBr^2.PtBr^4 + 12H^2O$	0·6974	114° 12′
$MnBr^2.PtBr^4 + 12H^2O$	0·7025	113° 53′
$ZnBr^2.PtBr^4 + 12H^2O$	0·6989	114° 6′
$CoBr^2.PtBr^4 + 12H^2O$	0·6970	114° 10′

The *calcium salt* has the same amount of water, and crystallises in small crimson ill-defined crystals.

Chlorides. When a solution of platinic chloride, freed from nitric acid by heating with hydrochloric acid, is evaporated over sulphuric acid and lime, large brown-red very deliquescent crystals are obtained, consisting of the *acid chloride*, *hydroplatinic chloride*, or *hydrogen platinochloride*, $H^2PtCl^6 + 6H^2O$ or $2HCl.PtCl^4 + 6H^2O$ (R. Weber, *Pogg. Ann.* cxxxi. 443).

Fuming nitric acid added to not very acid solutions of platinic chloride throws down the greater part of the platinum as a yellow precipitate, which when drained on an asbestos filter, and dried on a porous plate over sulphuric acid, forms a brownish-yellow deliquescent powder. This substance dissolves in water with evolution of nitrogen dioxide; but is decomposed by potash, with formation of nitric acid and without evolution of gas. Weber (*ibid.* 441) represents this compound by the formula $PtCl^4.2NO^2Cl + H^2O$; it is probably identical with that which Boyé and Rodgers obtained (iv. 668) by evaporating platinic chloride with nitromuriatic acid.

Platinochlorides.—Topsöe (*Jahresb.* 1868, p. 273) has prepared the following platinochlorides by adding weighed quantities of the corresponding oxides or carbonates to solution of acid platinic chloride, ($PtCl^4.2HCl + 6H^2O$), and evaporating over sulphuric acid at ordinary temperatures. The *barium salt*, $BaCl^2.PtCl^4 + 4H^2O$, crystallises in monoclinic prisms, $\infty P\infty . oP . \infty P . P$, sometimes tabular from predominance of the orthopinacoïds, and having the clinodiagonal, orthodiagonal, and principal axis in the proportion of 0·948 : 1 : 1·48, and the angle of the inclined axes = 77° 40′. The *calcium salt*, $CaCl^2.PtCl^4 + 8H^2O$, forms light yellow, warty or laminar, somewhat deliquescent crystals. The *lead salt*, $PbCl^2.PtCl^4 + 3H^2O$, crystallises in hard light yellow cubes, decomposed by a large quantity of hot water, with separation of lead chloride; according to Birnbaum, the crystals contain $4H^2O$, have an orange-red colour, effloresce over sulphuric acid, but deliquesce in the air, and dissolve easily in water and in alcohol.

The platinochlorides of the magnesium group have the general formula $M''Cl^2.PtCl^4 + 6H^2O$. They are very soluble—the cupric salt very deliquescent—but nevertheless crystallise with facility. The more or less yellow crystals are combinations of a rhombohedron of the first order with a prism, usually predominating, of the second order; sometimes they exhibit a monoclinic or even quadratic aspect. Topsöe describes the following:

	Length of axis *c* ($a = 1$)	Terminal angle of primary rhombohedron
$MgCl^2.PtCl^4 + 6H^2O$	0·5169	127° 17′
$MnCl^2.PtCl^4 + 6H^2O$	0·5310	126° 10′
$FeCl^2.PtCl^4 + 6H^2O$	0·5144	127° 30′
$NiCl^2.PtCl^4 + 6H^2O$	0·5162	127° 22′
$CoCl^2.PtCl^4 + 6H^2O$	0·5140	127° 32′
$ZnCl^2.PtCl^4 + 6H^2O$	0·5169	127° 18′
$CdCl^2.PtCl^4 + 6H^2O$	0·5235	126° 46′
$CuCl^2.PtCl^4 + 6H^2O$	0·5219	126° 53′

The magnesium and manganese salts crystallise in this form only above 20°; at lower temperatures, in irregularly developed combinations of two rhombohedrons with a prism of the second order; these two salts are likewise isomorphous:

	Axis *c*	Terminal angle
$MgCl^2.PtCl^4 + 12H^2O$	0·7057	113° 40′
$MnCl^2.PtCl^4 + 12H^2O$	9·7073	113° 44′

From these results it appears that the double salts of platinic chloride are isomorphous with those of platinic bromide containing the same quantities of water, also with the double fluorides of tin, titanium, zirconium, and silicium investigated by Marignac (*Jahresb.* 1859, p. 106; 1860, p. 134), and according to experiments by Jörgensen, cited by Topsöe, with the double salts of stannic chloride.

Silver chloride dissolves abundantly in concentrated solution of platinic chloride and crystallises out unaltered; but if to a perfectly neutral solution of platinic chloride mixed with a large quantity of ammonia, there be added, immediately after mixture, an ammoniacal solution of silver nitrate, a granular microcrystalline precipitate is formed, which, when dried over sulphuric acid, has the composition $Ag^2PtCl^6.2NH^3 + H^2O$. This compound treated with cold potash-ley gives off all its ammonia, and when boiled with sodium carbonate deposits all the silver and part of the platinum in the form of a dingy yellow precipitate, while the greater part of the platinum remains dissolved, forming a yellow solution from which, after acidulation with hydrochloric acid, the platinum may be precipitated as ammonium platinochloride. *Mercurous chloride* is decomposed by platinic chloride, with separation of mercury, and the solution yields on evaporation, first crystals of mercuric chloride, and afterwards a dark brown non-crystalline deliquescent mass (Birnbaum, *Zeitschr. f. Chem.* [2] iii. 520; *Bull. Soc. Chim.* [2] viii. 416).

Silver nitrate added to a solution of platinic chloride throws down the whole of the platinum in the form of a yellow precipitate of *argento-platinous chloride*, $AgCl.PtCl^2$, which does not blacken in sunshine, but slowly turns grey in diffused daylight. Mercurous nitrate forms with platinic chloride a light yellow precipitate quickly turning brown, whose proportional composition agrees with the formula $PtCl^2.2HgO.Hg^2Cl^2 + 5H^2O$; by fractional precipitation, compounds of permanent yellow colour are at length obtained. All these precipitates decompose, with separation of platinum, when heated with the liquid (platinum is also separated by precipitating from hot solutions) and dissolve in boiling nitric acid. When heated alone, they yield a sublimate of mercurous chloride, mercuric chloride, and mercuric oxide, together with water, and a residue of platinum. Platinic nitrate is not formed in the decomposition of platinic chloride by silver nitrate and mercurous nitrate (Commaille, *Bull. Soc. Chim.* [2] vi. 262).

On the reaction of platinic chloride with sulphurous acid, see SULPHITES.

Platinic Iodochloride, $PtCl^2I^2$, is formed by dissolving platinum in nitromuriatic acid, together with the quantity of iodine necessary to form platinic iodide, evaporating over the water-bath as long as acid fumes continue to escape, and leaving the solution to cool over sulphuric acid. It then separates in large brick-red prisms, which deliquesce in the air, and melt even below 100° to a red mobile liquid, smelling of iodine chloride when continuously warmed. The aqueous solution forms with chloride of potassium or ammonium a precipitate of potassium or ammonium platinochloride, whilst potassium or ammonium iodide remains in solution. It is coloured deep red by potassium iodide, and decomposed by iodine monochloride in the manner represented by the equation $PtCl^2I^2 + 2ICl = PtCl^4 + 2I^2$ (Kämmerer, *Ann. Ch. Pharm.* cxlviii. 329).

Diplatinocarbonyl tetrachloride. $(CO)^2Pt^2Cl^4 = COPtCl^2.C^2O^2PtCl^2$ (?).—This compound is formed when a mixture of chlorine and carbon monoxide is passed over spongy platinum heated to dull redness in a glass tube; it then sublimes as a yellow powder which must be immediately enclosed in dry glass vessels. This powder appears to contain different compounds, according to the temperature and other circumstances of the preparation, inasmuch as its melting point is found to vary from 130° to 150°. It dissolves easily in warm carbon tetrachloride, and separates in shining needles on cooling. When quickly and strongly heated, it is decomposed, giving off carbon monoxide and carbon oxychloride, and leaving platinum. As it decomposes nearly at the temperature at which it volatilises, it cannot be distilled, excepting in a stream of gas. It blackens in contact with moist air, and is instantly decomposed by water, with formation of carbon monoxide and dioxide, hydrochloric acid, and metallic platinum (Schützenberger, *Ann. Ch. Phys.* [2] xv, 100; *Zeitschr. f. Chem.* [2] iv. 321; *Jahresb.* 1868, p. 277).

PLATINUM-BASES, AMMONIACAL. The following observations on these compounds have been made by Hadow (*Chem. Soc. J.* [2] iv. 345). *Tetrammonio-platinous chloride* (diplatosamine hydrochloride) is conveniently prepared by digesting platinous chloride (obtained by heating platinic chloride) at a gentle heat with moderately strong ammonia, and evaporating the solution; the salt then crystallises in prisms containing $N^4H^{12}PtCl^2 + H^2O$. A hot solution of this salt yields with hot moderately concentrated nitric acid, a crystalline deposit of tetrammonio-platinic nitrato-chloride (diplatinamine chlorhydronitrate; Gros' nitrate), $N^4H^{12}Pt^{iv}(NO^3)^2Cl^2$, which by recrystallisation from water may be obtained in flat shining prisms. By boiling the solution of this salt for some hours with excess of silver nitrate (190 pts. to 460 pts. of Gros' nitrate) and a small quantity of nitric acid, it is converted into octammonio-diplatinic nitratoxychloride, $N^8H^{24}Pt(NO^3)^4OCl^2$ (iv. 676):

$$2N^4H^{12}Pt(NO^3)^2Cl^2 + 2AgNO^3 + H^2O = 2AgCl + 2HNO^3 + N^8H^{24}Pt^2(NO^3)^4OCl^2.$$

From the solution of this last salt, sal-ammoniac throws down a crystalline precipitate having the composition $N^8H^{24}Pt^2Cl^6O$.

The *di-ammonio-* and *tetrammonio-platinous compounds* possess, like platinous chloride, the power of reducing permanganates. The tetrammonio-platinous salts are further characterised by their behaviour to platinous chloride, with which they form the green salt of Magnus (iv. 674). The latter may be regarded as the type of a class of salts in which the platinous chloride, $PtCl^2$, is replaced by equivalent quantities of other chlorides, $HgCl^2$, $CdCl^2$, $PdCl^2$, $SnCl^2$, $CuCl^2$. The tetrammonio-salts are further distinguished from the diammonio-salts by the characteristic blue or green colorations or precipitates produced in their solutions by nitrous acid (*vid. inf.*).

The *ammonio-platinic salts* do not reduce permanganates. Sal-ammoniac added to solutions of tetrammonio-platinic and octammonio-diplatinic salts not containing chlorine (salts of diplatinamine), throws down an insoluble hydrochloride; tetrammonio-platinic nitrate forms with sodium sulphate a crystalline precipitate made up of needles. Ammonio-platinic salts containing chlorine (chloroplatinamine salts) are not precipitated either by sal-ammoniac or by sodium sulphate; the nitrate is characterised by its behaviour with platinous chloride, which when added to its solution acidulated with nitric acid, throws down a coppered-coloured precipitate of variable composition; ammonio-platinic compounds not containing chlorine do not exhibit this reaction. The di- and tetrammonio-platinic salts are reduced by sulphurous acid to the corresponding ammonio-platinous salts. This copper-coloured salt is likewise produced when the green salt of Magnus is digested for some hours with an excess of a very dilute and strongly acid solution of octammonio-diplatinic nitratoxychloride (Raewsky's nitrate). Its composition may be represented by the general formula $xN^2H^6PtCl^2.NO^2$. By boiling with water it is resolved into the green salt of Magnus, tetrammonio-platinic nitrato-chloride (Gros' nitrate), and platinic chloride.

Hadow has examined two of the compounds formed on passing nitrous acid into solutions of tetrammonio-platinous salts. A strongly acidulated solution of the nitrate thus treated yields a smalt-blue precipitate, composed of microscopic dodecahedrons; a similar solution of the hydrochloride yields a green precipitate, composed of microscopic feathery stars. The composition of the blue compound may be represented (empirically) by the formula $N^4H^{12}Pt(NO^3)^2.N^2O^4$; that of the green compound by $2N^4H^{12}PtCl^2.N^2O^3.2HCl$. Both these salts may be dried at 100° without decomposition, and dissolve in water with their original colour.

P. F. Cleve (*Acta Societatis Scientiarum Upsaliensis*, 1866; *Bull. Soc. Chim.* [2] vii. 12; *Jahresb.* 1867, p. 321) has examined a large number of salts belonging to the tetrammonio-platinous and tetrammonio-platinic series. From the fact that the platinic may be produced from the platinous compounds by direct oxidation, or direct addition of bromine, chlorine, &c., and the former from the latter by reduction, he infers that the compounds of these two series contain the same radicle, viz. $N^4H^{12}Pt^{iv}$, the oxide of the former series being $N^4H^{12}PtO$, that of the latter $N^4H^{12}PtO^2$.

Buckton (*Chem. Soc. Qu. J.* v. 213), by treating tetrammonio-platinous chloride with various metallic salts, obtained compounds of this chloride with the corresponding metallic chlorides; thus by mixing concentrated solution of tetrammonio-platinous chloride with acetate or nitrate of lead, a white crystalline precipitate is formed, which dissolves in hot water, and separates from the saturated solution in four-sided nacreous laminæ, consisting of the double chloride, $N^4H^{12}PtCl^2.PbCl^2$. It is insoluble in alcohol and in hydrochloric acid, and does not decompose at 170°. With solutions of mercuric chloride, zinc chloride, and cupric chloride, the compounds $N^4H^{12}PtCl^2.HgCl^2$, $N^4H^{12}PtCl^2.ZnCl^2$, and $N^4H^{12}PtCl^2.CuCl^2$, are obtained, all of which crystallise in laminæ. The copper-compound, which is yellow, is decomposed by boiling water into tetrammonio-platinic chloride, which separates, and cuprous chloride, which remains in solution; and on concentrating this solution and adding alcohol, a greenish precipitate is formed, consisting of the double chloride, $2N^4H^{12}PtCl^2.Cu^2Cl^2$, which may also be formed by direct combination of the two constituent chlorides.

A class of salts isomeric with those just described has recently been discovered by Thomsen (*Oversigt over det Kongl. danske Videnskabernes Selskabs Forhandlinger*, 1867, p. 225; *Jahresb.* 1867, p. 278). They are formed when a solution of ammonio-platinous chloride, or of platinous chloride itself, is precipitated by the ammoniacal solution of a metallic salt. They are all crystallisable (mostly in long prisms), and usually coloured, the copper salt being violet, the nickel salt green, the cadmium salt orange-coloured, the zinc salt red, and the silver salt light rose-coloured. They all, excepting the silver salt, withstand a temperature of 120°, but decompose when more strongly heated, giving off sal-ammoniac, hydrochloric acid, and nitrogen, and leaving a residue of platinum and metallic chloride. In water and ammonia they are nearly or quite insoluble, but dissolve easily in hydrochloric acid, being thereby distinguished from the double chlorides obtained by Buckton, which dissolve easily in water, but with difficulty in hydrochloric acid. The cupric salt of this series was obtained some years ago by Millon a. Commaille (iv. 675), by adding platinic chloride to a concentrated ammoniacal solution of cuprous chloride. On neutralising its alcoholic solution with ammonia, the whole of the copper is precipitated as oxychloride, and the solution saturated with hydrochloric acid and left to evaporate, leaves ammonio-platinous chloride. If this copper salt suspended in water be treated with a quantity of hydrogen sulphide not sufficient to decompose it completely, the liquid becomes strongly alkaline from the presence of free ammonia, and if it be then filtered from the copper sulphide and neutralised with hydrochloric acid, it likewise yields crystallised ammonio-platinous chloride. From this reaction, and from its mode of formation, Thomsen assigns to the copper salt the formula $PtCl.2NH^4Cl.N^2H^4Cu''$. The relations of these isomerides are inferred from the following considerations. A solution of tetrammonio-platinous chloride, $N^4H^{12}PtCl^2$ or $2NH^4Cl.N^2H^4Pt$, forms with an acid solution of cupric chloride, a precipitate of Buckton's copper salt, and with a solution of platinous chloride, a precipitate of the green salt of Magnus. Thomsen accordingly represents Buckton's salts as $CuCl^2.2NH^4Cl.N^2H^4Pt''$, &c., and the salt of Magnus as $PtCl^2.2NH^4Cl.N^2H^4Pt$, the latter being intermediate between the salts of Buckton and of Thomsen, as shown by the following comparison:

Buckton's Salts.

$R''Cl^2.2NH^4Cl.N^2H^4Pt''$. Soluble in water; insoluble in hydrochloric acid.

Salt of Magnus.

$Pt''Cl^2.2NH^4Cl.N^2H^4Pt''$. Insoluble in water; insoluble in hydrochloric acid.

Thomsen's Salts.

$Pt''Cl^2.2NH^4Cl.N^2H^4R''$. Insoluble in water; soluble in hydrochloric acid.

The general formula of all these compounds is therefore $R''Cl^2.2NH^4Cl.N^2H^4Q''$, in which R or Q, or both of them, may consist of platinum.

A comprehensive theory of the constitution of the ammoniacal platinum-compounds has lately been proposed by Odling (*Chem. News*, xxi. 289): *1.* The diammonio-platinous compounds are represented (as in Gerhardt's scheme, iv. 678) as containing the base *platosamine*, $Pt''(H^3N)^2$; and the diammonio-platinic compounds as containing the base *platinamine*, $R^2Pt^{iv}(H^3N)^2$, the symbol R denoting a monad chlorous radicle, Cl, HO, NO^3, &c.

2. The tetrammonio-compounds, platinous and platinic, are supposed to contain the bases *amoplatosamine*, $Pt''(H^5N^2)^2$, and *amoplatinamine*, $R^2Pt^{iv}(H^5N^2)^2$, these bases containing the monad radicle ammonio-amidogen, H^5N^2 or $H^3N.H^2N$, related to amidogen, H^2N, in the same way as the monad radicle ethyl, H^5C^2 or $H^2C.H^2C$, is related to methyl, H^3C. The parallelism between these two series of nitrogen and carbon compounds may be illustrated by the following formulæ of methyl chloride, ethyl chloride, sal-ammoniac, and ammonio-chloride of silver:

$$H^3C.HCl \qquad \left.\begin{matrix}H^2C\\H^2C\end{matrix}\right\}\begin{matrix}H\\Cl\end{matrix} \quad \Bigg| \quad H^3N.HCl \qquad \left.\begin{matrix}H^3N\\H^3N\end{matrix}\right\}\begin{matrix}Ag\\Cl\end{matrix}$$

The ammoniacal platinous and platinic compounds may therefore each be divided into the two groups of amic and ammonamic compounds. A fifth class is formed by the octammonio-platinic compounds, which contain the radicle *amo-diplatinamine*,

$R^4\overset{iv}{Pt}{}^2(H^6N^2)^4$. The following table exhibits the constitution of the principal ammoniacal platinum-compounds, formulated according to this scheme:

PLATINUM-BASES AND SALTS.

Platosamine.	*Amo-platosamine.*
$Pt''(H^2N)^2.2HCl$	$Pt''(H^5N^2)^2.2HCl$ + aq.
$Pt''(H^2N)^2.2H(HO)$	$Pt''(H^5N^2)^2.2H(HO)$
$Pt''(H^2N)^2.2H(NO^3)$	$Pt''(H^5N^2)^2.2H(NO^3)$
Platinamine.	*Amo-platinamine.*
$Cl^2Pt^{iv}(H^2N)^2.2HCl$	$Cl^2Pt^{iv}(H^5N^2)^2.2HCl$
$Cl^2Pt^{iv}(H^2N)^2.2H(HO)$?	$Cl^2Pt^{iv}(H^5N^2)^2.2H(NO^3)$
$(HO)^2Pt^{iv}(H^2N)^2.2H(HO)$	$(HO)^2Pt^{iv}(H^5N^2)^2.2H(NO^3)$
$OPt^{iv}(H^2N)^2.2H(NO^3)$ + 3aq. ?	$(NO^3)^2Pt^{iv}(H^5N^2)^2.2H(NO^3)$
$(NO^3)^2Pt^{iv}(H^2N)^2.2H(NO^3)$	$(NO^3)^2Pt^{iv}(H^5N^2)^2.2HCl$

$$\textit{Amo-diplatinamine}\ \text{(Raewsky's, \&c.)}\ldots\left\{\begin{array}{l} Cl^2O\overset{iv}{Pt}{}^2(H^5N^2)^4.4HCl \\ Cl^2O\overset{iv}{Pt}{}^2(H^5N^2)^4.4HNO^3 + aq. \\ (NO^3)^2\overset{iv}{Pt}{}^2(H^5N^2)^4.4HNO^3 + aq. \end{array}\right.$$

Odling has also obtained the base or hydrate of the platosamine series, $Pt''(H^2N)^2.2H(HO)$, by treating the hydrochloride with sulphuric acid, whereby it is converted into the sulphate, and decomposing this salt with baryta-water. It is extremely soluble in water, and readily crystallisable; yields a strongly alkaline solution; liberates ammonia from its salts; neutralises acids; absorbs carbonic acid from the air; and decomposes metallic salts, the resulting precipitates being however for the most part double compounds.

On the constitution of the platinum-bases, and of metallammonium compounds in general, see also Blomstrand (*Deut. chem. Ges. Ber.* iv. 40; *Chem. Soc. J.* [2] ix. 189).

PLATINUM-METALS, SEPARATION OF. Two methods for the separation of these metals have been given by Wolcott Gibbs: 1. By the action of *alkaline nitrites* on the compounds of the chlorides of these metals with potassium chloride (*Sill. Am. J.* [2] xxxiv. 341; *Chem. News*, vii. 61, 73, 97; *Jahresb.* 1863, p. 294).—2. By the action of *luteo-cobaltic chloride* on these same double chlorides (*Sill. Am. J.* [2] xxxvii. 57; *Chem. News*, ix. 121; *Jahresb.* 1864, p. 287). The separation of rhodium from iridium, and of ruthenium from platinum, rhodium, and iridium, by the first of these methods is described in vol. v. pp. 103, 137.

On the separation of iridium and platinum from rhodium and ruthenium, see also Carey Lea (*Sill. Am. J.* [2] xxxviii. 81, 248; *Chem. News*, x. 279, 301; xi. 3, 13; *Jahresb.* 1864, p. 290).

Bunsen has described a new method of working up the platinum-residues obtained (in the Russian Mint)—after separating the platinum from the nitro-muriatic solution of the ore with potassium chloride—by treating the mother-liquor with metallic iron in order to precipitate the other metals. This precipitated residue contains all the platinum metals except osmium, and is particularly rich in rhodium, which may be advantageously prepared from it by the process described (*Ann. Ch. Pharm.* cxlvi. 265; *Bull. Soc. Chim.* [2] xi. 508; *Zeitschr. f. Chem.* [2] v. 3, *Jahresb.* 1868, p. 280; *Phil. Mag.* [4] xxxvi. 253; *Chem. News*, xxi. 39).

POLYCHROÏTE. See SAFFRON.

PORPHYRINE. A base obtained by O. Hesse (*Ann. Ch. Pharm. Suppl.* iv. 40), together with chlorogenine, from a peculiar Australian bark. To prepare these bases, the strongly bitter concentrated aqueous extract of the bark is acidulated with sulphuric acid and mixed with mercuric chloride, which throws down the chlorogenine; and from the filtrate, freed from mercury by hydrogen sulphide, the porphyrine is obtained by neutralising with ammonia, precipitating the evaporated liquid with sodium carbonate, and agitating with ether; and purified by treating the ethereal solution with dilute sulphuric acid, again precipitating with sodium carbonate, extracting with ether, and decolorising with animal charcoal. On evaporating the ether, the porphyrine remains in the form of a varnish soluble in water and in alcohol, and partly crystallising from alcohol in thin white prisms. The solutions have an alkaline reaction and a very bitter taste. Porphyrine melts at 82°, and resolidifies in the amorphous state. With strong nitric acid it exhibits a characteristic red colour. With sulphuric and hydrochloric acids it forms neutral salts, whose solutions, like those of quinine salts, exhibit a deep blue fluorescence when slightly acidulated. The sulphate is easily soluble in water and in alcohol, and crystallises in thin prisms; the hydriodide, mercurochloride, platinochloride, and aurochloride are yellow or white precipitates. In the solution of the acid sulphate, potassium dichromate produces a blood-red colour, which subsequently disappears, with formation of a yellow precipitate.

PORPHYROXINE. This base, which is a constituent of opium, dissolves in strong sulphuric acid containing nitric acid, to a black-brown liquid, becoming dark garnet-red at 150° (Dragendorff, *Jahresb.* 1864, p. 727).

PORPHYRY. The porphyritic rocks of the island of Hochland, in the Gulf of Finland, have been chemically examined by J. Lemberg (*Arch. für die Naturkunde Liv.-, Ehst.- und Kurlands* [1] iv. 172, 337; *Jahresb.* 1867, p. 1015); the quartz-porphyrite of Monte Boccho in the Val San Pellegrino, by Tschermak (*Wien. Akad. Ber.* lv. [1] 287; *Jahresb.* 1867, p. 1022).

POTASSIUM. According to Baumhauer (*J. pr. Chem.* cii. 123), the oxidation of potassium on freshly-cut surfaces is attended with a faint luminosity visible in the dark.

Vogel (*Zeitschr. anal. Chem.* vii. 221) and Landolt (*ibid.* 20) have observed that potassium carbonate volatilises to a considerable extent at a strong red heat, and hence loss may arise in analytical processes, such as the valuation of tartar by ignition and titration of the residue, or in determining the quantity of ash yielded by plants, especially those which, like beet and sugar-cane, yield ashes consisting mainly of potassium carbonate.

For the preparation of pure caustic potash (or soda), Graeger (*J. pr. Chem.* xcvi. 188) first heats the solution of the alkaline carbonate with silver carbonate to remove chlorine, and then renders it caustic by means of burnt marble. The filtration of the caustic solution may be conveniently effected through pounded marble, freed from the finest dust by washing with water.

Potassium Iodide.—On the preparation of this salt, see Fuchs (*Dingl. pol. J.* clxxx. 251; *Jahresb.* 1865, p. 162; also Mich. Pettenkofer, *Pogg. Ann.* cxxviii. 459; *Jahresb.* 1866, p. 152). On certain of its properties: Payen (*Compt. rend.* lxi. 466; *Jahresb.* 1865, p. 162).

SULPHIDES.—According to Schöne (*Pogg. Ann.* cxxxi. 380), the only definite sulphides of potassium that can be obtained in the dry way are the *mono-*, di-, tri-, and pentasulphide. The other polysulphides described by Berzelius appear to be merely mixtures, and the formation of one or the other sulphide depends in general, not so much on the use of particular reagents, or on the mode of preparation, as on the temperature. When potassium monosulphide or carbonate is fused with excess of sulphur in a porcelain crucible, and the heat continued at a uniform temperature till the weight becomes constant, the product formed at the lowest possible temperature (not above 600°) is the pentasulphide, at a dull red heat (up to 800°) the tetrasulphide, at a bright red heat (to 900°) the trisulphide. If the alkaline carbonate, instead of the sulphur, be used in excess, trisulphide is formed also at the lowest of the above temperatures. By passing vapour of carbon bisulphide over red-hot potassium sulphate, Schöne obtained, not the tetrasulphide which is said by Berzelius to be formed under these circumstances, but lower compounds, approximating in composition to K^4S^7. When vapour of carbon bisulphide is passed over fused potassium carbonate, the sulphocarbonate is formed in the first instance, according to the equation:

$$2K^2CO^3 + 3CS^2 = 3CO^2 + 2K^2CS^3;$$

and this at a higher temperature is resolved into a mixture of carbon and trisulphide: $2K^2CS^3 = C^2 + 2K^2S^3$. In the wet way the following compounds were obtained:

The *monosulphide* crystallises from a solution of potash half saturated with hydrogen sulphide and evaporated in a vacuum, in deliquescent, four-sided prisms modified by truncations and sometimes tabular. The composition of these crystals, which are formed most readily at low temperatures, corresponds to the formula $K^2S.5H^2O$ or $K^2H^2SO.4H^2O$; they appear to be identical with the compound designated by Berzelius as crystallised sulphydrate (*Gmelin's Handbook*, iii. 31). In a vacuum or when heated to 150°, they leave the hydrate $K^2S.2H^2O$; at a higher temperature they appear to give up all their water without loss of hydrogen sulphide.

Hydrated Potassium Sulphydrate, $2KHS.H^2O$, separates from a solution perfectly saturated with hydrogen sulphide, by evaporation in a vacuum, in well-defined, colourless, transparent rhombohedrons, with shining surfaces. They are deliquescent, do not alter in a vacuum, or when heated to about 170°, but give off their water of crystallisation between 175° and 200°, retaining their form but losing their transparency. The anhydrous sulphydrate melts at a dull red heat to a very mobile yellowish liquid, which gradually becomes darker, and solidifies on cooling to a flesh-coloured cake having a crystalline structure. The solutions of the sulphydrate have an alkaline reaction, and give up half their sulphydric acid with tolerable facility when boiled. The solution of the monosulphide, even when it contains free alkali, is likewise slowly decomposed at the boiling heat, and appears ultimately to leave pure potassium hydrate, according to the equation: $K^2H^2SO + H^2O = H^2S + 2KHO$.

The *polysulphides* were obtained by boiling the solutions of the monosulphide or sulphydrate with the calculated quantity of sulphur in vessels from which air was excluded.—The *tetrasulphide* crystallises by evaporation in a vacuum in thin orange-red laminæ containing $K^2S^4.2H^2O$, very hygroscopic, easily soluble in water, less soluble in alcohol. When heated, they first melt in their water of crystallisation, afterwards give it off, finally also hydrogen sulphide and sulphur, and leave a fused brown residue. The hydrate $K^2S^4.8H^2O$ separates as a brownish oil on adding alcohol of 90 p. c. to a concentrated solution of the tetrasulphide or pentasulphide, in the latter case with separation of sulphur, which is taken up by the sulphide remaining in the alcoholic solution. The oil just mentioned yields, in contact with absolute alcohol, prismatic crystals apparently consisting of the preceding hydrate. The *pentasulphide* was not obtained in the solid state. Schöne finds that its solution is decomposed by prolonged boiling, with formation of hydrogen sulphide and potassium hyposulphite, probably according to the equation $K^2S^5 + 3H^2O = 3H^2S + K^2S^2O^3$, and that at the boiling heat it still takes up sulphur, which separates on cooling in microscopic octohedrons soluble in carbon bisulphide.

PROPANE. C^3H^8. *Propyl Hydride.*—This hydrocarbon, the third member of the marsh-gas or paraffin series, is gaseous in the free state at ordinary temperatures, and occurs among the gases evolved from the petroleum springs of North America (Ronalds, *Chem. Soc. J.* [2] iii. 529. Lefevre, *Zeitschr. f. Chem.* [2] v. 185. Fouqué, *ibid.* 304). It is formed: 1. By the action of fuming hydriodic acid on several hydrocarbons or their derivatives (Berthelot, *Jahresb.* 1867, pp. 344, 346):

$$\underset{\text{Iodopropylene.}}{C^3H^5I} + 3HI = C^3H^8 + 2I^2$$

$$\underset{\text{Benzene.}}{C^6H^6} + 10HI = 2C^3H^8 + 5I^2$$

$$\text{or } \underset{\text{Benzene.}}{2C^6H^6} + 6HI = 2C^3H^8 + C^6 + H^2 + 3I^2$$

$$\underset{\text{Toluene.}}{C^7H^8} + 2HI = C^3H^8 + C^4 + H^2 + I^2$$

$$\underset{\text{Cumene.}}{C^9H^{12}} + 6HI = 2C^3H^8 + C^3 + H^2 + 3I^2.$$

Phenol heated with hydriodic acid is reduced to benzene, which is then further converted into propane as above. Acetone yields propane, together with ethane and methane (Berthelot).

2. From secondary propyl iodide by the action of zinc and dilute hydrochloric acid:

$$\begin{array}{l}CH^3\\CHI\\CH^3\end{array} + H^2 = HI + \begin{array}{l}CH^3\\CH^2\\CH^3.\end{array}$$

Propane prepared by the last process may be purified by washing it successively with fuming sulphuric acid, with a mixture of sulphuric and nitric acid, and with soda-ley. If it be then collected over a strong solution of common salt, mixed with chlorine not in excess, and exposed to diffused daylight, an oily liquid is obtained containing a mixture of chlorinated derivatives of propane, which may be separated by fractional distillation. The lowest fraction, boiling at 42°-46°, consists of normal propyl chloride, $CH^3—CH^2—CH^2Cl$. On heating this liquid to 200° for several hours with potassium acetate and glacial acetic acid, and decomposing the resulting acetic ether with potash-ley in sealed tubes at 120°, normal propyl alcohol, $CH^3—CH^2—CH^2OH$, is obtained, which when oxidised by chromic acid, yields nothing but propionic acid. The propyl alcohol may be isolated by treating the alcoholic distillate obtained by the action of potash on the acetate, with potassium carbonate, whereupon a light oily liquid rises to the surface; and this, when dehydrated with potassium carbonate and anhydrous baryta boils between 80° and 90°, and may be separated by fractional distillation into a portion boiling between 80° and 85°, and another between 92° and 96°. The latter is the normal propyl alcohol; the former appears to be an acetal, $C^6H^{14}O^2$. The series of reactions above described affords a general method of converting a secondary alcohol into the normal primary alcohol.

The chief product of the action of chlorine on propane is ordinary propylene chloride, $C^3H^6Cl^2$, boiling between 94° and 98°. This chloride may be converted in the usual way into a glycol, yielding by oxidation carbonic and acetic acids, and therefore having the constitution of the already known propylene glycol, $CH^3—CHOH—CH^2OH$. It appears from these experiments that propane reacts with chlorine differently from ethane; for the latter is thereby converted into ethylidene chloride, $CH^3—CHCl^2$, in which both atoms of chlorine are attached to the same carbon-atom, whereas in propane the two hydrogen-atoms which are replaced by chlorine belong to different atoms of carbon (Schorlemmer, *Proc. Roy. Soc.* xvii. 372; *Ann. Ch. Pharm.* cl. 159).

The product of the action of chlorine on propane likewise contains more highly chlorinated compounds boiling between 100° and 200°. The latter are obtained in greater quantity by exposing the portion of liquid which boils above 80° to the further action of chlorine in direct sunshine for several days. The product is a liquid boiling between 120° and 200°, which by fractional distillation yields trichlorhydrin or trichloropropane, $C^3H^5Cl^3$, boiling between 150° and 160°. This liquid heated with dry potassium hydrate yields glycidic dichloride, $C^3H^4Cl^2$, which unites directly with bromine, forming the compound $C^3H^4Cl^2Br^2$. Hence it appears that propane and ethane differ also in the nature of their third chlorinated derivatives, propane yielding trichlorhydrin, the structure of which is most probably represented by the formula $CH^2Cl—CHCl—CH^2Cl$, whereas ethane yields the compound $CH^3—CCl^3$. It is further to be observed that the substitution-products of primary propyl chloride are identical with those of the secondary chloride; for, as Linnemann has shown (*Ann. Ch. Pharm.* cxxxvi. 48; cxxxix. 17), when chlorine is passed into secondary propyl iodide (v. 891), secondary propyl chloride is first formed, then probably propylene dichloride, and finally trichlorhydrin.

Tetrachloropropane, $C^3H^4Cl^4$, is obtained by exposing the liquid from which the trichlorhydrin has separated, to sunshine for several days, and then distilling. The product boils between 200° and 250°, and the portion distilling between 200° and 205° solidifies in the receiver to a crystalline mass of tetrachloropropane, which may be freed from an adhering oily chloride by pressure between paper, and obtained in stellate groups of small needles by recrystallisation from a hot-saturated alcoholic solution. It smells strongly like camphor, volatilises somewhat quickly when exposed to the air, melts when heated in a test-tube, and sublimes very rapidly; in a sealed capillary tube it melts at 177° to 178°, and resolidifies completely at 176° to 175°.

Hexchloropropane, $C^3H^2Cl^6$, is slowly produced by the action of chlorine in the brightest sunshine, and in presence of iodine, on the portion of the above-mentioned distillate which boils between 205° and 250°. It is a colourless liquid, smelling like camphor, and boiling without decomposition at 250°. It does not appear possible to replace more than six of the hydrogen-atoms of propane by chlorine (Schorlemmer, *Proc. Roy. Soc.* xviii. 29; *Ann. Ch. Phys.* clii. 159).

PROPARGYLIC ETHER. $C^5H^8O = \left.\begin{matrix}C^3H^3\\C^2H^5\end{matrix}\right\}O$ (Liebermann, *Ann. Ch. Pharm.* cxxxv. 266; *Jahresb.* 1865, p. 496).—Produced by the action of potassium ethylate on bromallylene; $C^3H^4Br + C^2H^5.H.O = HBr + C^3H^3.C^2H^5.O$; more readily by the prolonged action of boiling alcoholic potash on tribromallyl, $C^3H^5Br^3$. The distillate, freed from a brominated oil by washing with water, yields with ammoniacal silver-solution a white bulky precipitate of *argentopropargylic ether*, $\left.\begin{matrix}C^3H^2Ag\\C^2H^5\end{matrix}\right\}O$ (iv. 728), which when treated with acids yields propargylic ether. This ether is a liquid having an offensive odour, boiling at 72°, forming a white precipitate with silver solution, yellow with ammoniacal cupric chloride. The silver-compound resembles that of allyene, but has a stronger odour and is amorphous; melts and detonates when heated, leaving a pyrophoric mass; and forms a silver-speculum when boiled with water. Mixed with a solution of iodine in potassium iodide, as long as decoloration ensues, and then distilled, it yields a transparent, colourless, fetid oil consisting of *iodopropargylic ether*, $\left.\begin{matrix}C^3H^2I\\C^2H^5\end{matrix}\right\}O$. The silver-compound mixed with a large excess of iodine in ethereal solution forms a viscid yellowish oil, $\left.\begin{matrix}C^3H^2I.I^2\\C^2H^5\end{matrix}\right\}O$, which gives off iodine when heated. Iodopropargylic ether unites with bromine, forming the yellowish oily body $\left.\begin{matrix}C^3H^2I.Br^2\\C^2H^5\end{matrix}\right\}O$.

Propargylic ether may also be prepared by boiling trichlorhydrin with 3 pts. of potassium hydrate and a large quantity of alcohol. The alcoholic distillate yields with silver nitrate a dazzling white crystalline precipitate of the silver-compound $C^3H^2Ag.C^2H^5.O$, from which propargylic ether is easily obtained by the action of nitric acid, less easily by treatment with excess of potash, a pungent silver-blackening substance being then likewise formed, probably acrolein (Baeyer, *Ann. Ch. Pharm.* cxxxviii. 196).

By treating tribromallyl with a solution of potash in methyl alcohol, and the distillate with ammoniacal silver nitrate, the silver-derivative of *methyl-propargylic ether*, $\left.\begin{matrix}C^3H^2Ag\\CH^3\end{matrix}\right\}O$, is obtained, as a lemon-yellow gelatinous precipitate, from which, by the action of iodine dissolved in potassium iodide, the compound $\left.\begin{matrix}C^3H^2I\\CH^3\end{matrix}\right\}O$ is obtained, as an oil which solidifies in needles at about 12° (Liebermann). See further, Liebermann a. Kretschmer (*Ann. Ch. Pharm.* clviii. 230; *Chem. Soc. J.* [2] ix. 527).

PROPIODIACETAMIDE, $C^7H^{14}N^2O^3 = N^2(C^3H^5O)(C^2H^3O)^2H^3$ or $N(C^3H^5O)(C^2H^3O)H.N(C^2H^3O)H^2$, is formed by heating propionitrile and acetic acid in molecular proportions to 200° for a few hours (Gautier, p. 525).

PROPIONE. $C^5H^{10}O = CO(C^2H^5)^2$.—This ketone is formed by the oxidation of diethoxalic acid with potassium dichromate and sulphuric acid:

$$C^6H^{12}O^3 + O = CO^2 + H^2O + C^5H^{10}O.$$

It may be prepared by decomposing ethyl diethoxalate with potash, and, after distilling off the alcohol, treating the crude potassium diethoxalate with the oxidising mixture (Chapman a. Smith, *Chem. Soc. J.* [2] v. 173; *Jahresb.* 1867, p. 453). It is also produced, together with ethylcrotonic acid, by heating ethyl diethoxalate with fuming hydrochloric acid to 150° for several hours (Geuther, *Jahresb.* 1867, p. 455):

$$\underset{\text{Ethyl diethoxalate.}}{8C^6H^{11}(C^2H^5)O^3} + 8HCl + H^2O = \underset{\text{Propione.}}{3C^5H^{10}O} + \underset{\text{Ethyl-crotonic acid.}}{2C^6H^{10}O^2} + \underset{\text{Ethyl chloride.}}{8C^2H^5Cl} + \underset{\text{Alcohol.}}{8C^2H^6O} + 5CO^2.$$

The propione obtained by either of these processes is identical in properties with that obtained by the methods of Morley, Freund, and Wanklyn (iv. 729).—Propione, doubtless also identical with this, is formed by heating 1 pt. of bromamylene with 3·4 pts. mercuric oxide, 4 pts. glacial acetic acid, and sufficient water to ensure the solution of the mercuric oxide when heated. On distilling off about one-fourth of the product, neutralising the distillate with potash, again distilling off the most volatile portion, and mixing this distillate with water, a ketone, $C^5H^{10}O$, is obtained, which boils between 90° and 100°, and does not unite with acid sulphites of alkali-metal (Linnemann, *Zeitschr. f. Chem.* [2] iv. 57).

Isomeric with propione, and capable of uniting with alkaline bisulphites, are methyl-propyl ketone, boiling at 101°; methyl-isopropyl ketone, boiling at 93·5° (p. 768); ethyl-propyl aldehyde (b. p. 110°), from butyracetic acid (Limpricht a. von Uslar, *Jahresb.* 1855, p. 509); methyl-butyral (b. p. 110°), from calcium butyrate (Friedel, *ibid.* 1858, p. 295); and valeraldehyde (b. p. 101°).

PROPIONIC ACID. $C^3H^6O^2 = C^3H^5O.OH = CH^3—CH^2—COOH$.—This acid is formed: By reduction of iodopropionic acid with sodium-amalgam (Moldenhauer, *Jahresb.* 1864, p. 370); by heating methyl-crotonic acid with potash (Frankland a. Duppa, p. 829); and by heating argyræscin (from horse-chestnut bark) with potash (Rochleder, p. 59):

$$\underset{\text{Argyræscin.}}{C^{27}H^{42}O^{12}} + 2HKO = \underset{\text{Propionate.}}{C^3H^5KO^2} + \underset{\text{Æscinate.}}{C^{24}H^{39}KO^{12}}$$

It is also found amongst the products of the dry distillation of wood (Anderson, *Chem. News*, xiv. 257. Barré, *Zeitschr. f. Chem.* [2] v. 445).

Acetyl-propionic Acid. $C^5H^8O^3 = C^3H^4(C^2H^3O)O^2$.—The ethylic ether of an acid having this composition is produced by the action of ethyl chloracetate on the product of the action of sodium on ethyl acetate, and this ether boiled with caustic soda yields the corresponding *sodium salt*, $C^5H^7O^3Na$. The *zinc salt*, $(C^5H^7O^3)^2Zn$, and the calcium salt, $(C^5H^7O^3)Ca$, crystallise in colourless nacreous laminæ; the *silver salt*, $C^4H^7O^2Ag$, is slightly soluble in water (Noeldecke, *Zeitschr. f. Chem.* [3] iv. 681).

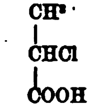
Bromopropionic Acid. $C^3H^5BrO^2$ (see iv. 733).—*Dibromopropionic acid*, $C^3H^4Br^2O^2$, is formed by direct addition of 1 mol. bromine to acrylic acid, $C^3H^4O^2$, in aqueous solution; it may be crystallised by very slow evaporation, but becomes resinous by keeping, and gives off hydrobromic acid. The bromine is only partially removed from it by boiling with baryta-water, and not completely even by silver oxide till after prolonged action (Wichelhaus, *Jahresb.* 1867, p. 403).

Chloropropionic Acid. $C^3H^5ClO^2$ (Wichelhaus, *Ann. Ch. Pharm.* clxiii. 1; cxliv. 351; *Jahresb.* 1867, p. 399).—This acid exists in two modifications, the one (α) produced by the action of water on lactyl chloride, $C^3H^4OCl^2$, or chloropropionyl chloride, $C^3H^4ClO.Cl$, the other (β) by the action of phosphorus pentachloride on glyceric acid.

α *Chloropropionic acid* was first obtained by Ulrich (iv. 733), but not in the pure state. Buchanan (*Zeitschr. f. Chem.* [2] iv. 523) prepares it by distilling calcium lactate with 2 mol. PCl^5, rectifying the product twice, collecting each time only the portion which boils above 111°, and mixing the resulting solution of lactyl chloride in phosphorus oxychloride with an equal quantity of water in a vessel cooled with water (not with ice). On subsequent distillation, the liquid separates into two layers, the upper of which distils over completely at 186°, and on subsequent rectification yields pure chloropropionic acid. Pure lactyl chloride free from phosphorus oxychloride is not completely decomposed by water, even after several hours' boiling.

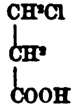
β Chloropropionic acid is prepared by treating a salt of glyceric acid with 3 mol. phosphorus pentachloride; distilling off the greater part of the phosphorus oxychloride (chloropropionyl chloride remaining in the residue); then connecting the retort with an upright condenser; gradually pouring in absolute alcohol; filtering off the separated phosphate; leaving the alcoholic filtrate to itself for 24 hours; and then mixing it with common salt, which throws down ethyl chloropropionate. This ether is freed from phosphoric ether by washing with water, rectified after drying, and decomposed by baryta-water; and the acid separated from the aqueous solution of the resulting barium salt by sulphuric acid, is dissolved by agitation with ether (Wichelhaus).

The difference of constitution between the two isomeric acids may be represented by the following formulæ:



$$\begin{array}{l} CH^3 \\ | \\ CHCl \\ | \\ COOH \end{array}$$

α Chloropropionic.



$$\begin{array}{l} CH^2Cl \\ | \\ CH^2 \\ | \\ COOH \end{array}$$

β Chloropropionic.

α Chloropropionic acid is a colourless transparent liquid, having a faint odour of acetic and butyric acids, and a sharp taste. It blisters the skin, mixes in all proportions with water, alcohol, and ether, boils at 186°, has a sp. gr. of 1·28 at 0°, and expands strongly by heat. It remains liquid at the temperature of a *mixture* of ice and salt (Buchanan). It forms a liquid chloride; its ethylic ether boils at 144°. It is easily decomposed by silver oxide, with formation of lactic acid; its barium salt is also decomposed when its solution is evaporated over the *water-bath*. Boiled with excess of silver oxide, it forms acetic and probably also formic acid (Wichelhaus).

β *Chloropropionic acid* forms fibrous tufts of crystals, smelling like *creosote*, melting and volatilising at 65°. Its chloride is crystalline. The ethylic ether boils at 150°–160°. The *barium salt* separates from its solution by evaporation over the water-bath in shining scales and laminæ. The acid is but slowly decomposed by silver oxide; when heated with excess of the oxide, it throws down metallic silver and forms carbacetoxylic acid, $C^3H^4O^4$, isomeric with malonic acid, but monobasic:

$$C^3H^5ClO^2 + 3Ag^2O = C^3H^3AgO^4 + AgCl + 2Ag^2 + H^2O.$$

The boiling point of α chloropropionic acid is the same as that of chloracetic acid: hence it cannot be homologous with the latter; the true homologue of chloracetic acid, $CH^2Cl—COOH$, is β chloropropionic acid, $CH^2Cl—CH^2—COOH$.

Iodopropionic Acid. $C^3H^5IO^2$.—There are two modifications of this acid, corresponding with those of chloropropionic acid, viz. the α acid obtained from lactic, and the β acid from glyceric acid.

α *Iodopropionic acid* is prepared by digesting syrupy lactic acid with 1 mol.

phosphorus di-iodide, pouring the mixture at the termination of the reaction into water, agitating with ether, and evaporating the ethereal solution. The acid then remains in the form of an oil nearly insoluble in water, whereas β iodopropionic acid, obtained by the action of hydriodic acid or of phosphorus iodide on glyceric acid (iv. 733), crystallises easily and well (Wichelhaus, *loc. cit.*).

β *Iodopropionic acid* boiled with silver oxide not in excess, yields a silver salt, convertible by double decomposition into a zinc salt, having the composition $(C^3H^5O^3)^2Zn$, and the properties of ordinary zinc lactate; but the mother-liquor after a while deposits crusts easily soluble in water and in alcohol, and having nearly the composition of the zinc salt of paralactic or sarcolactic acid. Wichelhaus regards the latter as the primary product of the transformation of β iodopropionic acid, and supposes that it is afterwards converted into ordinary lactic acid by prolonged boiling with the silver oxide; he thence infers that α chloro- and α iodo-propionic acid are analogous in constitution to ordinary lactic acid; β chloro- and iodopropionic acid to paralactic acid:

$CH^3—CHI—CO^2H$ α Iodopropionic.	$CH^2I—CH^2—CO^2H$ β Iodopropionic.
$CH^3—CH(OH)—CO^2H$ Lactic.	$CH^2(OH)—CH^2—CO^2H$ Paralactic.

Wislicenus (*Zeitschr. f. Chem.* [2] iv. 683) also finds that β iodopropionic acid boiled with recently precipitated silver oxide, yields lactic acid, and is of opinion that the acid $C^{12}H^{22}O^{11}$, called *hydracrylic acid*, which Beilstein obtained from β iodopropionic acid by the same process, was in all probability nothing but lactic acid.

Socoloff, on the other hand (*ibid.* v. 423), has obtained by similar means an acid, $C^3H^6O^3$, some of the salts of which differ in character from those of either of the known lactic acids, and from those of the isomeric methyl-glycollic acid. This acid he designates as *glyceraldehydic acid*, regarding it as the aldehyde of glyceric acid. Beilstein's hydracrylic acid he regards as an anhydride of this acid. (See LACTIC ACID, p. 770.)

β Iodopropionic acid heated with excess of *metallic silver* is converted into adipic acid, $C^6H^{10}O^4$ (Wislicenus, *ibid.* 680):

$$2(CH^2I—CH^2—CO^2H) + Ag^2 = 2AgI + [CO^2H—(CH^2)^4—CO^2H].$$

Phenyl-propionic Acid. $C^9H^{10}O^2 = C^6H^5(C^3H^5O^2)$.—Syn. with HYDROCINNAMIC ACID. See CINNAMIC ACID (p. 468). Under the same head are also described the chlorine, bromine, and iodine derivatives of phenyl-propionic acid, also of oxyphenyl-propionic or phenyl lactic acid, $C^9H^{10}O^3$.

Nitrophenyl-propionic acid, $C^9H^9(NO^2)O^2 = C^6H^4\left\{\begin{matrix}NO^2\\C^3H^5O^2\end{matrix}\right.$, is formed by treating hydrocinnamic acid with fuming nitric acid in a cooled vessel; when purified by separation from its sodium salt and recrystallisation from hot water, it forms feathery groups of faintly yellow crystals, very slightly soluble in cold, more easily in warm water, moderately soluble in alcohol and ether. It softens when heated, melts completely at 153°, and solidifies to a radio-crystalline mass on cooling. Its salts are for the most part easily soluble and difficult to crystallise; the lead and silver salts are yellowish precipitates. The acid oxidised with chromic acid mixture is converted into paranitrobenzoic acid: hence it belongs to the para series.

Amidophenylpropionic acid, $C^9H^9(NH^2)O^2 = C^6H^4\left\{\begin{matrix}NH^2\\C^3H^5O^2\end{matrix}\right.$, is formed, together with hydrocarbostyrol (p. 715), by treating the nitro-acid with tin and hydrochloric acid, and remains in the mother-liquor after the hydrocarbostyrol has been separated. It crystallises in groups of quadratic prisms, melting at 131° and decomposing at higher temperatures. It unites both with bases and with acids; but the salts which it forms with bases are unstable and difficult to crystallise. Its combinations with acids, on the other hand, crystallise well: the *hydrochloride*, $C^9H^{11}NO^2.HCl$, in groups of four-sided prisms; the *sulphate*, $2C^9H^{11}NO^2.H^2SO^4$, from water, in large nodular groups; from alcohol it is precipitated by ether in silky needles; the *nitrate* separates from solution in warm dilute nitric acid in fine crystals.

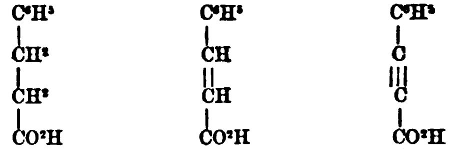
Chloride of Diazophenylpropionic acid, $C^9H^9N^2O^2Cl = C^6H^4\left\{\begin{matrix}N{=}NCl\\C^3H^5O^2\end{matrix}\right.$, is produced by passing nitrous acid vapour to saturation into a solution of *dry* hydrochloride of amidophenylpropionic acid in absolute alcohol, and crystallises in four-sided needles which detonate when heated. Their aqueous solution when warmed gives off large quantities of nitrogen, and the remaining liquid contains paraoxyphenylpropionic acid, $C^6H^4\left\{\begin{matrix}OH\\C^3H^5O^2\end{matrix}\right.$, identical with hydroparacoumaric acid (p. 716):

$$C^9H^9N^2O^2Cl + H^2O = C^9H^9(HO)O^2 + HCl + N^2.$$

Parabromophenyl-propionic acid, $C^9H^9BrO^2$, produced by the action of bromine on hydrocinnamic acid (p. 468), is converted by oxidation into parabromobenzoic acid.

Phenyl-propiolic Acid. $C^9H^6O^2$ (Glaser, *Zeitschr. f. Chem.* [2] iv. 328).—This acid, related to phenyl-propionic acid in the same manner as stearolic to stearic acid, is produced by the action of sodium and carbon dioxide on monobromocinnamene; also by abstraction of HBr from α-bromocinnamic acid, $C^9H^7BrO^2$, by means of alcoholic potash. (β-bromocinnamic acid treated in this manner yields an oily acid, p. 463.) It crystallises from water or from carbon bisulphide in long white silky needles melting at 136°–137°, and subliming at the same temperature in slender needles. Under water it melts at 80° to a colourless oil, which dissolves on further heating. The acid dissolves easily in ether, and still more in alcohol. The *barium salt*, $(C^9H^5O^2)^2Ba$, crystallises by slow evaporation in square tables containing 1 mol. H^2O; by evaporation over sulphuric acid in needles containing $2H^2O$; and from a solution cooled to a low temperature, in tufts of needles containing $3H^2O$. By boiling either of these hydrates with absolute alcohol, the anhydrous salt is obtained as a pulp of needle-shaped crystals. The anhydrous salt begins to decompose at 115°, and at higher temperatures gives off a yellowish oil (acetenyl-benzene ?). The *potassium salt*, $C^9H^5O^2K$, is a crystalline powder very soluble in water. The *silver salt*, $C^9H^5O^2Ag$, is a very sparingly soluble precipitate; the *lead salt*, a white amorphous precipitate; the *copper salt*, a blue precipitate consisting of small laminæ; with *ferric chloride* a yellow precipitate is obtained.

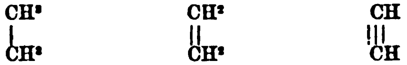
The relations between phenyl-propionic, cinnamic, and phenyl-propiolic acids are exhibited by the following formulæ:



$$\begin{array}{ccccc} C^6H^5 & & C^6H^5 & & C^6H^5 \\ | & & | & & | \\ CH^2 & & CH & & C \\ | & & \| & & ||| \\ CH^2 & & CH & & C \\ | & & | & & | \\ CO^2H & & CO^2H & & CO^2H \end{array}$$

Phenyl-propionic. Cinnamic. Phenyl-propiolic.

being similar to those between ethane, ethylene, and ethine or acetylene:



$$\begin{array}{ccccc} CH^3 & & CH^2 & & CH \\ | & & \| & & ||| \\ CH^3 & & CH^2 & & CH \end{array}$$

Ethane. Ethylene. Ethine.

PROPIONIC ALDEHYDE. $C^3H^6O = C^2H^5.COH$.—Rossi (*Compt. rend.* lxx. 129) has obtained this compound by the dry distillation of a mixture of the calcium salts of formic and propionic acids (the latter prepared from ethyl cyanide). The distillate, after drying with calcium chloride, yielded by fractional distillation, $\frac{2}{3}$ of its weight of pure propionic aldehyde,* a small quantity of butyric aldehyde, and a liquid boiling at 80°–100°, which apparently was not an aldehyde. Propionic aldehyde is a clear mobile liquid, having a pungent odour, boiling at 49·5° under a pressure of 740 mm., and having a sp. gr. of 0·8047 at 0°. According to Pierre a. Puchot, propionic aldehyde prepared by oxidation of normal propyl alcohol boils at 46°, and has a sp. gr. of 0·8329 at 0°, 0·8201 at 9·7°, and 0·7906 at 32·6°. Propionic aldehyde dissolves in water, but not in all proportions. It oxidises readily in the air, reduces ammoniacal silver solution, dissolves in acid sodium sulphite, but without separation of crystals, and is decomposed by heating with potash. By the action of water and sodium-amalgam it is reduced to normal propyl alcohol (Rossi).

PROPIONITRILE. See ETHYL CYANIDE, under CYANIDES (p. 524).

PROPIONYL BROMIDE. C^3H^5OBr.—Produced by gradually adding 2 mol. PBr^3 to 3 mol. propionic acid in a cooled retort, and subsequently distilling. When purified by repeated rectification, it is a fuming liquid having a peculiar odour resembling that of acetic acid, and also that of salted meat. Sp. gr. 1·465 at 14°. Boiling point 96°–98°. With water it becomes hot and is converted into propionic and hydrobromic acid (Sestini, *Bull. Soc. Chim.* [2] xi. 468).

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* The statement of Siersch (*Ann. Ch. Pharm.* cxlii. 115) that propionic aldehyde is not formed by this reaction, and consequently that the method cannot be employed for the synthetic production of the primary alcohols, is therefore disproved.

PROPIONYL IODIDE. C^3H^5OI.—Obtained by adding 19·6 pts. iodine by small portions to a mixture of 11·1 pts. propionic acid and 1·6 pt. dry phosphorus, cooling and agitating, then distilling, rectifying over phosphorus, and finally decolorising the distillate by agitation with mercury. It boils between 127° and 128°, sinks in water, and is immediately decomposed thereby (Sestini, *loc. cit.*).

PROPYL ALCOHOLS and **ETHERS.** 1. *Normal Propyl Alcohol*, $CH^3{-}CH^2{-}CH^2OH$, was first obtained, though not quite pure, by Chancel in 1853, from the fusel-oil of the residues left in the distillation of brandy from wine: he found it to boil at 96° to 97° (about 19° higher than ethyl-alcohol). Chancel has lately subjected propyl alcohol obtained from the same source to further examination (*Compt. rend.* lxviii. 659, 726); he now finds that it boils at 97°–100°, but that a very small quantity of water lowers the boiling point considerably. Sp. gr. 0·813 at 13° (water at 4° = 1). It forms a hydrate, $C^3H^8O.H^2O$, boiling constantly at 87·5° (under a pressure of 738 mm.), but decomposed by potassium carbonate. The alcohol is insoluble in cold concentrated solution of calcium chloride, and turns the plane of polarisation to the left; $[\alpha] = -5°$. By oxidation with chromic acid, it is almost wholly converted into propionic acid; if the quantity of the oxidising agent is comparatively small, propionic aldehyde, C^3H^6O, is likewise formed. Pierre a. Puchot (*Compt.* lxvi. 302) by distilling fermented beet-molasses, obtained, towards the end of the distillation, a mixture of amyl, butyl, and propyl alcohols. The propyl alcohol separated therefrom by fractional distillation boils at 98·5°, and is therefore also normal propyl alcohol. It has a sp. gr. of 0·820° at 0°, 0·812 at 10·3°, 0·780 at 51·1°, and 0·749 at 840°. The propyl iodide obtained from it boils at 104·5°, the acetate at 105°. Fittig, König, a. Schäffer (*Zeitschr. f. Chem.* [2] iv. 44) have demonstrated the existence of the same alcohol in a commercial fermentation-product designated as propylic alcohol and containing also amylic and ethylic alcohols. This liquid treated with bromine and phosphorus yielded a mixture of bromides from which, by fractionation, propyl bromide was obtained boiling at 71° to 71·5°. This therefore is normal propyl bromide, for its boiling point differs from that of ethyl bromide by the same amount (29°) as that of ethyl bromide (42°) differs from that of methyl bromide (13°). Hence the alcohol in question is normal propyl alcohol. Chapman a. Smith (*Chem. Soc. J.* [2] vii. 198) also, by subjecting the mixture of alcoholic bromides prepared from a fusel-oil of unknown origin to fractional distillation, obtained a propyl bromide boiling at 70·3° to 70·8°, and having a sp. gr. of 1·3532 at 26°. This bromide was converted into the corresponding acetate by treatment with potassium acetate and glacial acetic acid, and the acetate into the alcohol by heating it in a sealed tube with strong aqueous ammonia: the contents of the tube were neutralised with acetic acid and distilled, and the alcohol separated from the distillate by potassium carbonate. This alcohol boiled at 97°–98°, had a sp. gr. of 0·8120 at 16°, and yielded propionic acid by oxidation. The iodide, C^3H^7I, obtained from it by treatment with hydriodic acid boiled at 102°–103°, and had a sp. gr. of 1·7343 at 16°.

Schorlemmer, as already observed (p. 957), has obtained normal propyl alcohol from propane prepared by the action of zinc and hydrochloric acid on isopropyl iodide; this affords the means of converting isopropyl compounds into normal propyl compounds; the alcohol thus obtained (not quite pure) boiled at about 96°.

Linnemann (*Ann. Ch. Pharm.* cxlviii. 251) has prepared normal propyl alcohol from ethyl alcohol in the same manner as he formerly obtained ethyl alcohol from methyl alcohol, namely by converting it first into ethyl cyanide or propionitrile, then successively into propionic acid, propionyl chloride, and propionic anhydride (by heating the chloride with sodium propionate), and treating the anhydride with sodium-amalgam in the same manner as in the preparation of ethyl alcohol from acetic anhydride (p. 592). The propyl alcohol thus obtained boiled between 84° and 91°, and was therefore not quite pure. By oxidation with chromic acid it yielded propionic acid.

Lastly, Rossi (*Compt. rend.* lxx. 129; *Zeitschr. f. Chem.* [2] vi. 141) has obtained normal propyl alcohol by the action of nascent hydrogen on propionic aldehyde prepared from ethyl alcohol as already described (p. 962). The aldehyde was dissolved in 15–20 times its weight of water, sodium-amalgam was introduced into the liquid by small portions, and an equivalent quantity of sulphuric acid added at the same time. As soon as the liquid ceased to reduce silver-solution, it was distilled; the distillate was filtered to separate a few drops of an insoluble oily substance; and the propyl alcohol was separated from its aqueous solution by distillation and addition of potassium carbonate. The product amounted to $\frac{2}{3}$ of the theoretical quantity. Propyl alcohol thus obtained boils at 96° (bar. at 743 mm.), and has a sp. gr. of 0·8205 at 0°. By oxidation with chromic acid it yields pure propionic acid.

The following table exhibits the boiling points and specific gravities of the normal propyl alcohol and the corresponding ethers:

Normal Propylic Alcohol and Ethers.

	Boiling Point	Specific Gravity	Observer
Alcohol, C^3H^7OH .	96°–97°	0·813 at 13°	Chancel.
	98·5°	0·820 ,, 0° 0·812 ,, 10°	Pierre a. Puchot.
	96°	0·8205 ,, 0°	Rossi.
	84°–91°	—	Linnemann.
Chloride, C^3H^7Cl .	52°	—	Chancel.
	46·5°	0·9156 at 0°	Pierre a. Puchot.
Bromide, C^3H^7Br .	71·0°–71·5°	—	Fittig.
	70·3°–70·8°	1·352 at 16°	Chapman a. Smith.
	68°–72°	—	Linnemann.
	70°–71°	1·3887 at 0°	Rossi.
	72°	1·3497 ,, 0°	Pierre a. Puchot.
Iodide, C^3H^7I . .	99°–101°	1·637 ,, 75·3°	Chancel.
	102°–103°	1·7343 ,, 16°	Chapman a. Smith.
	102°	1·7821 ,, 0°	Rossi.
	101·5°	1·7102 ,, 2°	Linnemann.
	104·25°–104·5°	1·784 ,, 0°	Pierre a. Puchot.
Oxide, $(C^3H^7)^2O$ . .	85°–86°	—	Chancel.
Methylate, $\left.\begin{matrix}C^3H^7\\CH^3\end{matrix}\right\}O$.	49°–52°	—	,,
Ethylate, $\left.\begin{matrix}C^3H^7\\C^2H^5\end{matrix}\right\}O$.	68°–70°	—	,,
Amylate, $\left.\begin{matrix}C^3H^7\\C^5H^{11}\end{matrix}\right\}O$.	125°–130°	—	,,
Formate, $\left.\begin{matrix}C^3H^7\\CHO\end{matrix}\right\}O$.	82°	—	,,
	82·5°–83°	0·9197 at 0°	Pierre a. Puchot.
		0·8977 ,, 38·5	,, ,,
		0·836 ,, 72·5	,, ,,
Acetate, $\left.\begin{matrix}C^3H^7\\C^2H^3O\end{matrix}\right\}O$.	102°	—	Chancel.
	103°	0·910° at 0°	Pierre a. Puchot.
		0·8635 ,, 42·5	,, ,,
		0·8137 ,, 84·6	,, ,,
	100°–101°	0·913 ,, 0°	Rossi.
Propionate, $\left.\begin{matrix}C^3H^7\\C^3H^5O\end{matrix}\right\}O$	118°–120°	—	Chancel.
	124·3°	0·903 at 0°	Pierre a. Puchot.
		0·857 ,, 51·3°	,, ,,
		0·795 ,, 100·6°	,, ,,
Butyrate, $\left.\begin{matrix}C^3H^7\\C^4H^7O\end{matrix}\right\}O$.	139°–141°	—	Chancel.
	137·25°	0·888 at 0°	Pierre a. Puchot.
		0·841 ,, 47·25°	,, ,,
		0·785 ,, 100·25°	,, ,,
Valerate, $\left.\begin{matrix}C^3H^7\\C^5H^9O\end{matrix}\right\}O$.	157°	0·887 ,, 0°	,, ,,
		0·7915 ,, 100·15°	,, ,,
Cyanide, C^3H^7CN .	163°	0·977 ,, 0°	Rossi.

Isopropyl Alcohol. $CH^3—CHOH—CH^3$.—The formation of this alcohol from acetone, propylene, or glycerin has been already noticed (v. 889). It is also formed: *a*. By the action of nascent hydrogen on acrolein, C^3H^4O, and on propylene oxide, C^3H^6O (Linneman, *Ann. Ch. Pharm.* cxxxiii. 132: cxl. 178).—*β*. From ethyl alcohol, by converting the latter, first into ethyl cyanide or propionitrile, $CH^3—CH^2—CN$, then into propylamine, $CH^3—CH^2—CH^2—NH^2$, by the action of nascent hydrogen, and the latter into propyl alcohol by heating the aqueous solution of its nitrite (p. 63). This series of actions might rather be expected to yield normal propyl alcohol, $CH^3—CH^2—CH^2OH$; but the greater part of the alcoholic liquid obtained was found to boil at 83°–85°, and to yield acetone by oxidation: it was therefore isopropyl alcohol. A smaller portion boiled at 93°–96°, and appeared to be the same alcohol mixed with a small quantity of a foreign substance. The change of the propyl radicle from normal propyl, $CH^2CH^2CH^3$, into isopropyl, $CH(CH^3)^2$, probably takes place in the conversion of the propionitrile into propylamine. The formation of the alcohol is accompanied by that of a nitrogenous substance, $C^6H^{14}N^2O$, boiling between 200° and 205°, having a sp. gr. of 0·924 at 14°, and slightly soluble in water (Siersch, *Ann. Ch. Pharm.* cxliv. 137; see also Linnemann, *ibid.* cl. 370).—γ. Dichlorhydrin, $CH^2Cl—CHOH—CH^2Cl$, dissolved in ether free from alcohol, but not anhydrous, is converted by sodium-amalgam into isopropyl alcohol, mixed with products of higher boiling point (Buff, *Zeitschr. f. Chem.* [2] iv. 124).—δ. Glycolic iodhydrin, $C^2H^4I(OH)$, treated with zinc-methyl, yields the compound $\left.\begin{matrix}C^3H^7\\(CH^3Zn)'\end{matrix}\right\}O$, and this, when heated with water under pressure, is converted into isopropyl alcohol (Butlerow a. Ossokin, p. 64). Yssel de Schepper a. Tak (*ibid.* iv. 520) have obtained isopropyl alcohol from the portion of grain fusel-oil boiling at 93°–98°, by boiling it with potash in a flask with upright condenser and distillate. The distillate dehydrated with sodium carbonate yielded a propyl alcohol boiling at 83°–84°, and convertible into an iodide boiling at 72°–91°.

Isopropyl alcohol subjected to a series of processes exactly similar to that by which it is formed from ethyl alcohol, yields an alcohol, $C^4H^{10}O$, probably consisting of isobutyl alcohol (Siersch, *Ann. Ch. Pharm.* cxlviii. 261; *Jahresb.* 1868, p. 436).

The *haloïd isopropyl ethers*, formed by treating the alcohol with the corresponding hydracids, exhibit the following properties:

	Boiling point.	Sp. gr.
Isopropyl chloride . . .	36° to 38° at 741 mm.	0·874 at 10°
„ bromide . . .	60 „ 63° „ 739 „	1·320 „ 13°
„ iodide . . .	89 „ 90° „ 735 „	1·70 „ 15°

The action of bromine on isopropyl alcohol gives rise (inasmuch as acetone and hydrobromic acid are formed by abstraction of water) to isopropyl bromide, propylene bromide, and substitution-products of acetone, from which, by the action of potash, bromoform may be produced. Isopropyl chloride is but little attacked by chlorine or bromine. Isopropyl iodide is converted, by the action of chlorine or of hydrochloric acid and potassium chlorate, into a product boiling between 90° and 170°, from which, by fractional distillation, trichlorhydrin, $C^3H^5Cl^3$ (b. p. 154°–159°; sp. gr. 1·417 at 15°), may be separated. Bromine converts isopropyl iodide into the bromide. When equal volumes of bromine and isopropyl bromide are heated with water to 140°–150°, monobromisopropyl bromide, $C^3H^6Br^2$, is formed, together with further substitution-products. This compound is identical with propylene bromide, boils at 140°–143°, and has a sp. gr. of 1·954 at 150°. By silver acetate in presence of glacial acetic acid it is converted into propylene diacetate (b. p. 180°–185°), and by alcoholic potash into monobromopylene, C^3H^5Br (b. p. 56°–58°; sp. gr. 1·40 at 13°). This last compound unites with bromine, forming the compound $C^3H^5Br.Br^2$ (b. p. 194°–196°; sp. gr. 2·390 at 10°), identical with that previously obtained by Wurtz (*Jahresb.* 1857, p. 462) and by Cahours (*ibid.* 1850, p. 496). Heated with silver acetate and glacial acetic acid to 110°–120°, it is converted, as shown by the equation,

$$C^3H^5Br^3 + C^2H^3AgO = C^3H^4Br^2 + C^2H^4O^2 + AgBr,$$

into *dibromopropylene*, $C^3H^4Br^2$ (b. p. 127°–131°; sp. gr. 1·98 at 15°), which is identical with allylene bromide, inasmuch as, when treated with sodium, it gives off a gas exhibiting all the properties of allylene.

When isopropyl bromide and water are heated with 2 mol. bromine to 110°–120°, a colourless liquid is formed, which on distillation at 180° yields isopropyl bromide and propylene bromide, whilst the residue contains a mixture of more highly brominated substitution-products. After prolonged standing in the cold, it deposits a large quantity of crystallised *tribromisopropyl bromide*, $C^3H^4Br^3.Br$, while the expressed oily mother-liquor contains, in the portions boiling between 180° and 200°, *dibromisopropyl bromide*, $C^3H^5Br^2.Br$. This compound is converted by silver oxide into an easily soluble silver salt, an oily liquid insoluble in water, boiling above 150°, in ether, and especially in benzol. Heated with potash it yields potassium oxypicrate and ethylic alcohol (Stenhouse).

OXYQUINONE. $C^6H^4O^3 = C^6H^4\left\{\begin{matrix}O\\O\end{matrix}\right. O$ (Malin, *Ann. Ch. Pharm.* cxli. 345). —A compound produced by fusing rufigallic acid with potash:

$$C^7H^4O^4 + O = C^6H^4O^3 + CO^2.$$

On saturating the product with dilute sulphuric acid, agitating the filtered solution with ether, and leaving the ether to evaporate, oxyquinone is obtained in hydrated yellowish crystals containing $C^6H^4O^3.H^2O$. After being pressed to remove the brown mother-liquor, and recrystallised from boiling water, it forms soft straw-yellow microscopic needles, slightly soluble in cold, easily in boiling water, also in alcohol and ether, having a faint acid reaction, and not volatile. The aqueous solution when heated reduces silver nitrate and alkaline cupric solutions; in the dilute state it colours ferric chloride violet, afterwards blue-green. Oxyquinone, like quinone, has but slight combining tendencies; nevertheless it absorbs dry ammonia gas and forms a yellowish precipitate with lead acetate. It is not converted into quinone by nascent hydrogen.

OXYSULPHOBENZIDE. $C^{12}H^{10}SO^4 = \left.\begin{matrix}C^6H^5SO^2\\C^6H^5\end{matrix}\right\}O^2$ (Glutz, *Ann. Ch. Pharm.* cxlvii. 52; *Jahresb.* 1867, p. 635).—Produced by the action of strong sulphuric acid on crystallised phenol. It dissolves easily in boiling water, also in alcohol and ether, and crystallises therefrom in groups of thick needles, fusible at a moderate heat, decomposing at a higher temperature. It unites both with bases and with acids. Its *ammoniacal* solution deposits short prisms of the salt $C^{12}H^9(NH^4)SO^4$; the *sodium salt*, $C^{12}H^9NaSO^4$, forms short prisms easily soluble in water and in boiling alcohol. The *acetate*, $C^{12}H^8(C^2H^3O)^2SO^4$, obtained by heating oxysulphobenzide with excess of acetyl chloride to 130°, crystallises from alcohol in needles, decomposing at the boiling heat into oxysulphobenzide and acetic acid. *Nitro-oxysulphobenzide*, $C^{12}H^8(NO^2)^2SO^4$, crystallises in scales, and forms with the alkalis and alkaline earths easily soluble deep yellow compounds, *e.g.* $C^{12}H^6Na^2(NO^2)^2SO^4$ and $C^{12}H^6Ba(NO^2)^2SO^4$. By phosphorus iodide in presence of a little water, it is converted into the compound $C^{12}H^8(NH^2)^2SO^4.2HI$, which forms crystals easily soluble in water and in alcohol; caustic soda decomposes it, separating the corresponding base as a white precipitate quickly turning brown on exposure to the air.

OXYVALERIC ACID. $C^5H^{10}O^3 = C^4H^8(OH).CO^2H$. *Valerolactic Acid.*—Produced by heating bromovaleric acid with silver oxide and water, and purified by converting it into calcium salt, precipitating the latter with alcohol, converting it into zinc salt, and decomposing this salt with hydrogen sulphide. Crystallises by evaporation over sulphuric acid in large rectangular tables, not deliquescent, but very soluble in water, alcohol, and ether; melts at 80°, and volatilises with vapour of water, also at 100° in the air-bath. The *sodium salt*, $C^5H^9O^3Na$, the *calcium salt*, $(C^5H^9O^3)^2Ca + H^2O$, and the *zinc salt*, $(C^5H^9O^3)^2Zn$, are soluble in water and crystallisable. The *copper salt*, $(C^5H^9O^3)^2Cu + H^2O$, separates on mixing the calcium salt with cupric acetate, in light green prisms which become anhydrous at 170°. The *silver salt*, $C^5H^9O^3Ag$, is a bulky precipitate, separating from hot water in feathery crystals (Clark a. Fittig, *Ann. Ch. Pharm.* cxxxix. 199).

OZONE. Soret has determined the density of ozone by comparing its rate of diffusion with that of chlorine. His experiments confirm the result previously obtained by Andrews (iv. 301), that the density of ozone is 1½ time as great as that of ordinary oxygen (*Ann. Ch. Phys.* [4] xiii. 257; *Jahresb.* 1867, p. 123). Another, but less exact method, depending on the absorption of ozone by oil of turpentine, yielded results tending to the same conclusion (*Ann. Ch. Phys.* [4] vii. 113; *Jahresb.* 1865, p. 120).

On the properties of ozone and ozonides, see Schönbein (*J. pr. Chem.* xcv. 469; cii. 145, 155, 164; cv. 226; *Jahresb.* 1865, p. 121; 1867, p. 132; 1868, p. 136). On ozone and so-called *antozone*, see v. Babo a. Claus (*Ann. Ch. Pharm.* cxl. 348; *Jahresb.* 1866, p. 98); Weltzien (*Ann. Ch. Pharm.* cxxxviii. 129; *Jahresb.* 1866, p. 99); C. Hoffmann (*Pogg. Ann.* cxxxii. 607; *Jahresb.* 1867, p. 130).

P. J. Hollmann finds that 1 gram of ozone, in passing to the state of ordinary oxygen, gives off 355·5 units of heat (*Arch. néerland.* iii. 260; *Jahresb.* 1868, p. 136).

According to O. Loew (*Zeitschr. f. Chem.* [2] vi. 65, 269), ozone is produced in active as well as in slow combustion. Air which had passed through the flame of a Bunsen's burner smelt strongly of ozone, turned guaiac paper blue, and quickly separated iodine from potassium iodide.

On the existence of ozone in the air, see ATMOSPHERE (p. 233).

yellow laminæ or flattened needles, moderately soluble in water, somewhat soluble in a mixture of equal volumes of alcohol and ether (Gautier, *Compt. rend.* lxvii. 723).

Isopropylamine is also produced, together with di-isopropylamine, by distilling crude isopropyl cyanide (from isopropyl iodide and potassium cyanide) with hydrochloric acid. The two bases liberated from the resulting mixture of hydrochlorides (which is free from sal-ammoniac) are easily separated by distillation. Isopropylamine thus obtained boils at 31·5° under a pressure of 743 mm., and has a sp. gr. of 0·690 at 18°, converted by nitrous acid into isopropyl alcohol (Siersch, *Zeitschr. f. Chem.* [2] v. 145).

Di-isopropylamine, $NH(C^3H^7)^2$, is a transparent, easily inflammable liquid, slightly soluble in water, having a faint ammoniacal odour, and a soapy taste. Boils at 83·5° to 84° under a pressure of 743 mm. Sp. gr. 0·722 to 22°. The *hydrochloride* forms very deliquescent needles; the *platinochloride* large reddish-yellow tables, easily soluble in water and in alcohol, sparingly in ether-alcohol (Siersch).

PROPYLENE. C^3H^6.—This hydrocarbon is found among the products obtained by the action of 1 mol. zinc ethyl on 2 mol. allyl iodide (Wurtz, *Bull. Soc. Chim.* [1863] v. 51); it is also formed, together with ethyl bromide, by the action of zinc-ethyl on bromoform (Alexeyeff a. Beilstein, *ibid.* [2] ii. 51):

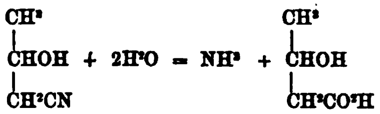
$$CHBr^3 + Zn(C^2H^5)^2 = C^3H^6 + C^2H^5Br + ZnBr^2.$$

According to Butlerow (*Ann. Ch. Pharm.* cxlv. 271), the propylene obtained from allyl iodide and hydriodic acid is identical with that formed by decomposition of amyl-alcohol, and has probably the constitution represented by the formula $CH^3—CH—CH^2$. Propylene from either of these sources is absorbed by hydriodic acid, forming isopropyl iodide, $CH^3—CHI—CH^3$, and exhibits one and the same reaction with hypochlorous acid. The same propylene is obtained by heating methylchloracetol, $CH^3—Cl^2—CH^3$, with sodium to 130°–150°; the gas thereby evolved forms with bromine a compound, $C^3H^6Br^2$, boiling at 141°–143°, and exhibiting all the properties of ordinary propylene bromide. But by treating acetone with phosphorus chlorobromide, PCl^3Br^2, a compound, $C^3H^6Br^2$, is obtained, boiling at 113° to 116°, and having a sp. gr. of 1·8149 at 0°. This bromide gradually dissolves in water at 160°, forming a liquid which smells like acetone, and when heated to 100° with silver benzoate, yields, together with benzoic acid, a body crystallising in the same form as that obtained by Oppenheim (*infra*) from the hydriodide of chloropropylene.

By potassium permanganate propylene is oxidised to acetic and formic acids (Truchot, *Compt. rend.* lxiii. 274); by a solution of crystallised chromic acid in a small quantity of water, it is converted into acetone, C^3H^6O (Berthelot, *Ann. Ch. Pharm.* cl. 373).

Propylene Chloride, $C^3H^6Cl^2$, formed, together with other products, by the action of chlorine on propane (p. 957), has the constitution $CH^3—CHCl—CH^2Cl$, and is convertible into ordinary propylene glycol, $CH^3—CHOH—CH^2OH$ (Schorlemmer).

Propylene Chlorohydrate, $(C^3H^6)''Cl(OH)$ or $CH^3—CHOH—CH^2Cl$, produced by direct combination of propylene with hypochlorous acid, is converted, by heating with potassium cyanide in sealed tubes, into the corresponding *cyanohydrate*, $(C^3H^6)''CyOH$, and this latter boiled with caustic potash is converted into an acid, $C^4H^8O^3$, isomeric with oxybutyric acid:



$$\begin{array}{l} CH^3 \\ | \\ CHOH \\ | \\ CH^2CN \end{array} + 2H^2O = NH^3 + \begin{array}{l} CH^3 \\ | \\ CHOH \\ | \\ CH^2CO^2H \end{array}$$

(Markownikoff, *Zeitschr. f. Chem.* [2] iv. 620).

Bromo- and *Chloro-propylenes.*—Monobromopropylene, C^3H^5Br (boiling at 56·5°, sp. gr. 1·408 at 19°), is converted by agitation with chlorine-water and mercuric oxide into monochloracetone:

$$2C^3H^5Br + HgCl^2O^2 = HgBr^2 + 2C^3H^5ClO.$$

Monochloropropylene (b. p. 23°; sp. gr. 0·918 at 9°) is converted into chloracetone by similar treatment. Monobromo- or monochloro-propylene heated for several days to 100° with mercuric acetate and glacial acetic acid, is converted into acetone (Linneman, *Ann. Ch. Pharm.* cxxxviii. 122).

Chloropropylene, C^3H^5Cl, treated with concentrated sulphuric acid, yields hydrochloric acid and a sulpho-acid (containing the residue C^3H^4) which when distilled

Palmitolic acid unites with 1 mol. *bromine*, forming the dibromide, $C^{16}H^{28}Br^2O^2$ (dibromo-hypogæic acid); with excess of bromine in sunshine (with partial decomposition and evolution of hydrobromic acid) it forms the tetrabromide, $C^{16}H^{28}Br^4O^2$ (tetrabromopalmitic acid), which crystallises from alcohol in light yellow laminæ.

Monobromopalmitolic acid, $C^{16}H^{27}BrO^2$, is produced by the action of boiling alcoholic potash on monobromo-hypogæic dibromide (p. 727) according to the equation:

$$C^{16}H^{29}Br^3O^2 + 2KHO = C^{16}H^{27}BrO^2 + 2KBr + 2H^2O.$$

It has been obtained only in an impure state, as a solid dark brown mass melting at 31°, heavier than water, soluble in alcohol and ether.

PALMITOXYLIC ACID, $C^{16}H^{28}O^4$, is produced, together with suberic acid and suberic aldehyde, by gradually adding fuming nitric acid to pamitolic acid, assisting the action at first by a gentle heat:

$$\underset{\substack{\text{Palmitolic}\\ \text{acid.}}}{2C^{16}H^{28}O^2} + 7O = \underset{\substack{\text{Palmitoxylic}\\ \text{acid.}}}{C^{16}H^{28}O^4} + \underset{\substack{\text{Suberic}\\ \text{acid.}}}{C^8H^{14}O^4} + \underset{\substack{\text{Suberic}\\ \text{aldehyde.}}}{C^8H^{14}O^2}$$

The suberic acid is dissolved out of the product by repeated boiling with water; the washed residue is dissolved in hot alcohol; and the lower dark-coloured oily layer of the filtrate, consisting chiefly of suberic aldehyde, is separated after cooling from the supernatant yellow solution of palmitoxylic acid. The crystalline mass which remains on evaporating this solution, when pressed between filtering-paper and recrystallised from hot absolute alcohol, yields pure palmitoxylic acid in iridescent yellowish laminæ, melting at 64°, insoluble in water, easily soluble in alcohol and ether. It is monobasic. The *silver salt*, $C^{16}H^{27}O^4Ag$, obtained from the sodium salt by precipitation, is white, nearly insoluble in water, turns dark violet when exposed to light, and may be heated to 150° without decomposition.

PANATOMS. G. Hinrichs has endeavoured to reduce the chemistry of the present day to a system of atomic mechanics, starting from the hypothesis that all the elements are formed of a single primary substance, pantogen, the atoms of which are regarded as material points, and as equal to one another. For the development of the system we must refer to the original treatise: *Atomechanik, oder die Chemie eine Mechanik der Panatome*, 4to, Iowa, 1867. A short abstract of it is given in the *Jahresbericht für Chemie*, 1867, p. 20.

PAPAVERINE. This base has been re-examined by Hesse (*Ann. Ch. Pharm.* cliii. 75), who prepares it from the precipitate P, obtained from aqueous opium extract, as described under OPIUM-BASES (p. 883). This precipitate digested with excess of oxalic acid yields crystalline oxalate of papaverine. It is better, however, first to dissolve the precipitate in acetic acid, remove thebaine by means of tartaric acid, precipitate the mother-liquor of the tartrate with ammonia, and treat the resinous precipitate with a small quantity of alcohol, whereby it is gradually converted into crystals, while an amorphous base passes into the solution. The crystals are dissolved in excess of oxalic acid, and the oxalate is purified by repeated crystallisation from boiling water, till it dissolves without colour in strong sulphuric acid. The oxalic acid is then removed by calcium chloride, and the base is precipitated by ammonia, and obtained pure by recrystallisation from hot alcohol.

Papaverine forms delicate colourless prisms, tasteless, without action on litmus, melting at 147°, turning reddish, and finally decomposing at a higher temperature. According to Merck (iv. 338), it assumes a deep blue colour when strong sulphuric acid is poured upon it. According to Hesse, on the other hand, pure papaverine dissolves without colour in strong sulphuric acid at ordinary temperatures, but the solution when heated becomes dark violet, like a similar solution of codamine or laudanine (pp. 480, 774). Papaverine which had not been completely purified by oxalic acid dissolved in strong sulphuric acid with very dark colour. Papaverine dissolves in acetic acid, but does not neutralise it; dilute sulphuric, nitric, or hydrochloric acid added to this solution, produces a milky turbidity and ultimate precipitation of the sulphate, nitrate, or hydrochloride of papaverine; the chlorides of sodium and calcium act in like manner, precipitating papaverine as hydrochloride; sodium nitrate precipitates the nitrate. With a solution of the acetate of a certain degree of dilution, the hydrochloride and nitrate are obtained in fine crystals. Potash and soda produce in the acetate solution a resinous precipitate, which soon becomes crystalline, and is insoluble in excess of the reagent.

Papaverine contains, according to the mean of Hesse's analysis, 71·77 p. c. carbon, 6·02 hydrogen, and 4·26 nitrogen, agreeing with the formula $C^{21}H^{21}NO^4$ (71·76 C, 5·98 H, and 3·99 N). Former analyses by Merck and Anderson (iv. 338) gave a smaller proportion of carbon (70·47–70·71 p. c.), leading to the formula $C^{20}H^{21}NO^4$. Hesse's analysis of several of the salts of papaverine gave results in accordance with his formula of the base. These salts dissolve in strong sulphuric acid without coloration.

The name *papaverine* has also been applied by Deschamps d'Avallon (*Ann. Ch. Phys.* [4] i. 453) to another base (better called pseudopapaverine), extracted from the dried capsules of *Papaver somniferum.* It is described as colourless, inodorous, bitter, acid to test-paper; more soluble in hot water than in cold; insoluble in ether and in chloroform; crystallising from alcohol in short nacreous needles; precipitated from solution in hydrochloric acid by mercuric chloride. A solution of iodine in potassium iodide colours it in aqueous solution blue, and forms a brown precipitate with the solution in hydrochloric acid.

PAPAVEROSINE. A substance obtained from the same dried poppy capsules, after exhaustion with water, by digesting them with alcohol of 56 p. c., treating the alcoholic extract with ether, dissolving the ethereal extract in hydrochloric acid, and repeatedly crystallising the base precipitated by magnesia from alcohol. It is colourless, inodorous, nearly tasteless, slightly alkaline; soluble in alcohol, ether, chloroform, hot olive oil, and benzol; does not crystallise from ether or chloroform, but separates from the other solvents in prisms apparently monoclinic. Strong sulphuric acid colours it violet, changing to red when heated, and to dark orange on addition of a little nitric acid. Its solution gives a whitish precipitate with platinic chloride; yellow with potassium chromate and with solution of iodine in potassium iodide; white with potassio-mercuric iodide, ammonium molybdate, barium peroxide, potassium ferrocyanide and ferricyanide (Deschamps, *loc. cit.*).

PARA. Respecting the meaning of this prefix in the Aromatic Series, see page 798.

PARABANIC ACID, $C^3H^2N^2O^3$, is obtained in crystals by heating uric acid with manganese dioxide and water, and gradually adding sulphuric acid as long as any action takes place (Wheeler, *Bull. Soc. Chim.* [2] vii. 521); also by heating uric acid with potassium or sodium nitrite, adding sulphuric acid, and evaporating over the water-bath (Gibbs, *Deut. chem. Ges. Ber.* 1867, p. 341). Parabanic acid heated with potassium permanganate in presence of sulphuric acid is ultimately converted into carbon dioxide and ammonia: $C^3H^2N^2O^3 + 2H^2O + O = 3CO^2 + 2NH^3$ (Gibbs).

PARACONIC ACID. An acid isomeric with itaconic acid, produced by heating itamonochloropyrotartaric acid with water. (See Itaconic Acid, p. 760.)

PARACOUMARIC ACID. $C^9H^8O^3$ (Hlasiwetz, *Ann. Ch. Pharm.* cxxxvi. 31).—This acid, isomeric with coumaric acid (p. 498), is extracted by ether from aloes previously exhausted with water containing sulphuric acid. After repeated crystallisation from weak spirit, with addition of animal charcoal, it forms sickle-shaped or furcate needles, slightly soluble in cold, more freely in boiling water, most easily in warm alcohol or ether. It is nearly tasteless, has a strong acid reaction; melts at 179°–180°; produces a dark golden-brown coloration with ferric chloride in alcoholic solution; does not reduce either silver nitrate or an alkaline cupric solution. It is monobasic and forms crystalline salts. $C^9H^7O^3(NH^4) + H^2O$ crystallises in monoclinic tables; $(C^9H^7O^3)^2Cd + 3H^2O$ in stellate groups of needles; $(C^9H^7O^3)^2Cu + 6H^2O$ in sparingly soluble greenish-blue needles; $C^9H^7O^3Ag$ is a white bulky precipitate.

Paracoumaric acid is converted by sodium-amalgam into hydroparacoumaric acid (p. 716), and by nitric acid, or by fusion with potash, into paraoxybenzoic acid, just as coumaric acid is converted into salicylic acid (p. 498).

PARADATISCETIN. $C^{15}H^{10}O^6$.—A compound isomeric with datiscetin (ii. 306) and luteolin, produced by fusing quercetin with potash, and separated, on supersaturating the fused mass with hydrochloric acid, as a flocculent substance, which crystallises from very weak spirit in yellowish needles. It dissolves easily and with acid reaction in dilute alcohol, less easily in ether, and is nearly insoluble in water; the alcoholic solution is coloured violet by ferric chloride, yellow by potash, turning green in contact with the air, red or red-brown by aqueous chlorine or bromine. Silver nitrate and alkaline cupric solution are reduced when heated with it. Boiled with the carbonates of alkaline earths, it yields hydrated salts, which crystallise in long needles; the barium salt dried at 100° is $(C^{15}H^9O^6)^2Ba + 2H^2O$; the strontium salt, $(C^{15}H^9O^6)^2Sr + 2H^2O$. Paradatiscetin fused with potash yields phloroglucin, but neither quercetic nor protocatechuic acid (Hlasiwetz a. Pfaundler, *J. pr. Chem.* xciv. 65; *Jahresb.* 1864, p. 563).

Nearly all proteids when in aqueous solution or suspension are found to change in character, especially in their solubilities. These changes are very marked at a temperature of about 40°. The preparation of most of the substances is tedious, and hence the results of the examination of apparently the same substance vary exceedingly.

The compounds they form with metallic salts and other bodies are variable in composition (those with potassio-platinic cyanide no less than others) (Diakonow, *Hoppe-Seyler's Untersuch.* ii. p. 228).

They all contain nitrogen, carbon, hydrogen, oxygen (sulphur and phosphorus) in the proportions given below. That the sulphur in proteids is unoxidised is shown by their giving off sulphuretted hydrogen when treated with strong alkalis, and in various other decompositions. The phosphorus is probably present as phosphates either mechanically attached or joined in some peculiar loose combination.

All proteid solutions are lævorotatory.

With one exception (peptones), all proteids diffuse with great difficulty.

Boiled with Millon's reagent* they all give a deposit which after a while turns red, the supernatant liquor also becoming coloured red. Heated with strong nitric acid they turn yellow, the mixture on addition of ammonia becoming a deep orange (xantho-proteic reaction).

They change the colour of the cupro-potassic test-liquid for sugar from blue to violet.

Proteids are very conveniently divided into classes as is done by Hoppe-Seyler (*Handbuch physiol. chem. Anal.*).

CLASS I. ALBUMINS.—Soluble in water.

1. **Egg-albumin.** *Preparation.*—The white of hen's egg is diluted with an equal bulk of water, well stirred, strained, treated with dilute acetic acid as long as any precipitate falls, filtered, carefully neutralised, and concentrated to the original bulk at a low temperature.

Characters.—A neutral, transparent, generally faintly yellowish fluid, turning the plane of polarisation to the left, the specific rotation being 35·5° for yellow light (sodium flame). Heated to about 70° the whole or greater part of the substance is thrown down as a flocculent or curdy precipitate. The supernatant liquid, always more alkaline than before, is generally opalescent, from the formation of *alkali*-albumin (see below).

By careful acidulation all proteid matter is thrown down, and a *perfectly clear* filtrate obtained.

The substance thus thrown down is not a mere precipitate. It differs radically in its characters from soluble albumin, is remarkable by its great insolubility, *and is* called *coagulated* albumin (see below.)

The exact temperature at which this coagulation by heat takes place is much affected by various circumstances, notably by the presence of neutral salines, which *lower the* point of coagulation.

Treated with excess of alcohol, egg-albumin is wholly precipitated from its solutions. If the alcohol be rapidly filtered off, the precipitate may be wholly or in great *part* redissolved in water. Within a short time, however, it is found that, under the influence of the alcohol, the precipitate passes into the coagulated state; the longer the alcohol is allowed to act, the greater is the proportion of the material coagulated.

By strong mineral acids, especially by nitric acid, egg-albumin is precipitated and coagulated.

Metallic salts, such as mercuric chloride, silver nitrate, lead acetate, give a precipitate containing variable quantities of the precipitant. The lead precipitate suspended in water, treated with sulphydric acid to remove the lead, and neutralised, gives a solution of albumin. The white of egg always contains saline matters, which are retained in the solution of albumin prepared as above. All attempts completely *to* remove these salines by dialysis, &c., have failed, and it is still an open question whether they in part are in some way intimately associated with the albumin, and whether their presence is not essential to its being in a state of solution.

2. **Serum-albumin.** *Preparation.*—Serum of blood is diluted with water, treated with dilute acetic acid as long as any precipitate appears, filtered, neutralised, and reduced to its original bulk at a low temperature.

Characters.—Thus prepared, serum-albumin agrees in its main features with egg-albumin. They differ in the following points:

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* *Millon's Reagent.*—Equal quantities of mercury and strong nitric acid are mixed and gently warmed till the mercury is dissolved. The solution is diluted with twice its bulk of water, and the copious precipitate allowed to settle. The clear supernatant liquid is the reagent.

The specific rotation of serum-albumin is 56° for yellow light.

Egg-albumin agitated with ether is coagulated. If the solution be dilute, the coagulum appears on standing at the junction of the two liquids. Serum-albumin is not coagulated by ether.

Egg-albumin is very readily coagulated by strong hydrochloric acid; the coagulum redissolves with very great difficulty. Serum-albumin is not so readily coagulated by the same acid; the coagulum redissolves readily.

CLASS II. GLOBULINS.—Insoluble in water, soluble in very dilute acids and alkalis, soluble in dilute (1 p. c.) solutions of sodium chloride and other neutral salts.

1. **Myosin.** *Preparation.*—Fresh muscle finely minced is rapidly washed with distilled water until the wash-water gives no signs of containing proteids or of being acid, and is then treated with a 10 or 5 p. c. solution of sodium chloride. The resulting viscid mass is strained through linen, filtered through coarse paper, and dropped little by little into a large quantity of distilled water. A large flaky precipitate is thus produced which settles on standing. The liquid is removed by decantation and filtration, the precipitate redissolved in the saline solution, filtered, and again precipitated with water.

Characters.—Insoluble in water. Readily soluble in sodium chloride solutions, of ·1 to 10 or more p. c. (also in other neutral saline solutions). From these solutions myosin is precipitated either by extreme dilution or by saturation. On adding the solid salt to a sodium chloride solution of myosin, the liquid becomes more and more viscid, and just as the point of saturation is reached, the whole of the myosin is precipitated. The precipitate may then be separated by filtration, and washed if necessary with saturated solution of the salt. The amount of salt still adhering to it is sufficient to render it capable of being dissolved when treated with distilled water.

Treated either by the method of dilution or of saturation, the myosin remains unchanged by the action of the reagents.

Exposed, however, either in solution or suspension for any length of time, especially at a temperature of 20°–40°, myosin changes in solubility, becoming less and less soluble in dilute neutral saline solutions. The same change may be brought about instantaneously by dilute acids or alkalis. Myosin is exceedingly soluble in dilute acids. The solutions are uncoagulated by boiling, indeed apparently unchanged. On neutralisation the whole of the proteid is thrown down; the acid solution is also precipitated by the addition of neutral salines. The precipitate, however, is no longer myosin; it is no longer soluble in dilute neutral saline solution; it has passed into Class III. In like manner myosin is extremely soluble in dilute alkalis; the whole of the dissolved proteid may be precipitated on neutralisation, but the precipitate is no longer soluble in dilute neutral salines; it too belongs to Class III.

Suspended in water and heated to 70°, myosin enters into the insoluble or coagulated condition. The neutral saline solutions of myosin are coagulated by heat.

Just as fibrin (see below) does not exist as such in living blood, so myosin does not exist as such in living muscle. It makes its appearance *pari passu* with the condition of muscle known as *rigor mortis* (of the mechanical phenomena of which it is most probably the cause), by a process similar to the coagulation of blood. If living, still irritable muscle, freed as much as possible from blood and lymph (the muscle of frog is most convenient for the purpose), be frozen, minced, mixed with snow containing 1 per cent. of sodium chloride, and powdered, at a temperature below freezing point, the mixture may with great care be filtered when melting. The filtrate speedily (at the temperature of the body almost immediately) sets into a gelatinous mass, which afterwards separates by contraction into a clot and serum. The clot, however, has the characters, not of fibrin, but of myosin.

2. **Globulin.** (*Paraglobulin.*) *Preparation.*—When fresh blood-serum is diluted tenfold with water, and a brisk stream of carbonic acid passed through it, a fine granular precipitate is formed, which may be separated by decantation and filtration, and washed with water.

It may also be prepared by saturating blood-serum with sodium chloride (or magnesium sulphate, &c.), as in the case of myosin. A certain amount of the salt will cling to the precipitate.

Characters.—Globulin is exceedingly soluble in dilute saline solutions (from which it may be precipitated unchanged by carbonic acid gas or *exceedingly* dilute acids). Insoluble in water, it is dissolved however when the water is saturated with oxygen.

concentric or arborescent groups of silky crystals. The acid dissolves easily in alcohol and ether, and in 272·5 pts. of cold water, melts at 187·5° to 188°, and sublimes in small transparent needles. Neutral or slightly acid solutions form a red-brown precipitate with ferric chloride (R. Peltzer, *Ann. Ch. Pharm.* cxlvi. 284; *Zeitschr. f. Chem.* [2] v. 225).

Dibromo-paraoxybenzoic Acid. $C^7H^4Br^2O^3$.—The ethylic ether of this acid separates on adding saturated bromine-water to an alcohol solution of ethylic paraoxybenzoate diluted with hot water, in white flocks which separate from alcohol in short shining needles (Barth, *J. pr. Chem.* c. 366).

Iodoparaoxybenzoic acids are produced by the simultaneous action of iodine and iodic acid on paraoxybenzoic acid; the best proportions are those indicated by the following equation:

$$10C^7H^6O^3 + 3IO^3H + 6I^2 = 5C^7H^5IO^3 + 5C^7H^4I^2O^3 + 9H^2O.$$

The paraoxybenzoic acid is dissolved in hot water in a flask provided with an upright condenser; iodine and iodic acid are added in powder; and the liquid is heated nearly to boiling for about five minutes, and then quickly filtered. Di-iodoparabenzoic acid then remains on the filter, while the mono-iodated acid, contaminated with a small quantity of paraoxybenzoic acid separates from the filtrate. The mono-iodated acid is purified by repeated crystallisation from hot water, with addition of animal charcoal: it first separates in granules, but when nearly pure, in small needles having a glassy lustre (Peltzer, *loc. cit.*). It is also produced, though not in the pure state, by heating paraoxybenzoic acid with potassium iodate and sulphuric acid: the product is a resinous mass which when fused with potash is resolved into potassium iodide and protocatechuic acid (Barth; Peltzer).

Monoiodoparaoxybenzoic acid, in the air-dried state, contains $2C^7H^5IO^3 + H^2O$, and gives off its water at 100°. It dissolves in 576 pts. of cold water, much more easily in hot water, very easily in alcohol and ether. It melts at 160°, decomposes at 192° (iodosalicylic acid does not melt below 196°); when very gradually heated it sublimes, much below its melting point, in silky needles two lines long. The aqueous solution forms a dingy brown precipitate with ferric chloride. The *monosodic salt*, $C^6H^3I(OH).CO^2Na$, formed by adding the acid to a hot solution of sodium carbonate in sufficient quantity to produce strong acid reaction, removing the excess of acid by ether, and strongly concentrating the remaining solution, crystallises in fine efflorescent monoclinic crystals, often concentrically grouped. The *disodic salt*, $C^6H^3I(ONa).CO^2Na + 5H^2O$, is obtained by adding the acid to excess of hot aqueous sodium carbonate, adding a large quantity of alcohol, and evaporating the filtered solution to dryness. On redissolving in absolute alcohol and evaporating in a vacuum, the salt is obtained in hygroscopic silky needles, having a neutral reaction, and giving off their water at 130°. The *barium salt*, $(C^7H^4IO^3)^2Ba + 7H^2O$, forms transparent rhombic tables having their prismatic edges truncated; becomes anhydrous at 100°. The use of an excess of barium carbonate does not give rise to a salt richer in barium. The *silver salt*, $C^7H^4IO^3Ag$, is a white pulverulent precipitate nearly insoluble in water, easily soluble in ammonia (Peltzer).

Di-iodoparaoxybenzoic acid, $C^7H^4I^2O^3 = C^6H^2I^2(OH).CO^2H$, is easily purified by boiling it several times with water, dissolving the residue in sodium carbonate, precipitating with hydrochloric acid, then dissolving in strong alcohol, decolorising with animal charcoal, and mixing the solution with a sufficient quantity of water to produce turbidity; the acid is then deposited on cooling in small colourless needles. It is nearly insoluble in boiling water; dissolves easily in alcohol and ether; decomposes when heated, without previous fusion; and cannot be sublimed. Its two *sodium salts* are prepared similarly to those of the mono-iodated acid. The salt $C^7H^3I^2O^3Na + 7H^2O$ forms tufts of delicate, iridescent, efflorescent needles. The *disodic salt*, $C^7H^2I^2O^3Na^2 + 6H^2O$, forms transparent rhombic tables: both are easily soluble in water. From these salts two corresponding *silver salts* are obtained as flocculent curdy precipitates detonating when heated. The *barium salt*, $C^7H^2I^2O^3Ba$, is separated by alcohol from its aqueous solution, as a gelatinous precipitate, which dries up to a very loose white powder. The *calcium salt*, $C^7H^2I^2O^3Ca + 2H^2O$, crystallises from concentrated solution in nacreous laminæ, easily soluble in cold water. The *lead salt*, $C^7H^2I^2O^3Pb$, is formed, as a bulky precipitate, with elimination of acetic acid, when a solution of the disodic salt is mixed with lead acetate; when heated it swells up like mercuric sulphocyanate. Both mono- and di-iodoparaoxybenzoic acid are easily reduced by sodium-amalgam to para-oxybenzoic acid. The di-iodated acid is but imperfectly decomposed by fusion with sodium carbonate, even at 200°; the fused mass assumes a flesh-red colour on exposure to the air (Peltzer).

(*e. g.* ·1 p. c.) in the form of acid-albumin, long known as *syntonin*. No characters are at present known by which syntonin or acid-albumin derived from muscle may be distinguished from other forms of acid-albumin.

Like the globulins, acid-albumin changes rapidly in character when left exposed for any time to ordinary temperature. It becomes less and less soluble in dilute acids, requiring for its solution a stronger acid or an increase of temperature.

2. **Albuminate** or **Alkali-albumin.**—If egg- or serum-albumin be treated with dilute caustic alkali instead of with acid, coagulation by heat is similarly prevented, and the whole of the proteid may in like manner be thrown down on neutralisation.

Alkali-albumin may also be prepared from albumin by the action of strong caustic potash, according to the method of Lieberkühn.

White of egg is treated with an equal bulk of water, filtered, and reduced to its original volume by evaporation in shallow vessels at a low temperature. Potassium hydrate is then added drop by drop, until the mixture becomes a gelatinous transparent mass. This is cut into small pieces and washed rapidly until the wash-water ceases to have an alkaline reaction. It is then dissolved in hot water, giving an apparently neutral solution, from which it may be thrown down by the addition of a dilute acid. There is of course an immense loss of substance. Contact with oxygen is to be avoided.

Albuminate is insoluble in water and in solutions of sodium chloride, readily soluble in dilute acids, dilute alkalis, and dilute solutions of alkaline carbonates. In all these characters it agrees with acid-albumin. From its alkaline solutions it is precipitated by saturation with magnesium sulphate, and the precipitate is soluble in water. Its effect on the polarised ray is variable. Serum albumin treated with strong alkali acquires a rotatory power of 86°, egg-albumin 47°, coagulated albumin 58°, the result being nevertheless in each case albuminate.

Albuminate is insoluble in cold alcohol, and may be precipitated from its solution by an excess of that agent; in hot (diluted) alcohol it is however more or less soluble, the amount being very much increased by the presence of free alkali.

From its acid or alkaline solutions it is precipitated on neutralisation; in presence of sodium phosphate the alkaline solution has to be rendered freely acid before the precipitation takes place.

In these respects it differs from acid-albumin. These do not, however, appear very certain, and probably albuminate dissolved in dilute acid becomes acid-albumin, and acid-albumin in an alkaline solution becomes albuminate. Like acid-albumin, albuminate in acid or alkaline solution is unchanged by boiling; suspended in water, however, and heated to 70°, it passes into the coagulated state.

The proteid substance casein exists in milk. From this it may be thrown down by the addition of acetic acid, especially after dilution. The best results are obtained by adding a very small quantity of acetic acid until the first appearance of a precipitate, and then passing a brisk stream of carbonic acid through the mixture. The precipitate thus gained, when freed from fat, is insoluble in water and in sodium chloride solutions, but is readily soluble in dilute acids and alkalis (and alkaline carbonates), and reprecipitable on neutralisation. In fact, it agrees in most respects with albuminate. It may also be prepared from milk by saturating with magnesium sulphate, washing the precipitate free of fat, and redissolving in water.

Two facts are however brought forward to distinguish casein from albuminate:

1. When casein is treated with caustic potash, potassium sulphide is produced: this is not the case with albuminate.—2. Casein digested with artificial gastric juice yields a body containing phosphorus, whereas an albuminate which contains no phosphorus can be prepared from white of egg (Lubavin, *Hoppe-Seyler's med.-chem. Unters.* 1871, 463).*

Prepared by means of magnesium sulphate, casein has a rotatory power of 80°, in dilute alkaline solution of 76°, in strong alkaline solution of 91°, in dilute acid solution of 87°. Casein then may be taken as a naturally occurring alkali-albumin, just as syntonin is the most commonly and easily produced acid-albumin. A natural form of alkali-albumin also occurs in blood-serum (*serum casein* of Panum) and other similar fluids, besides the globulin and albumin. It may be obtained by adding dilute acetic acid to blood-serum freed by carbonic acid from globulin. A similar substance has been described as existing in the protoplasm of nerve-centres and in plain muscular fibre.

CLASS IV. **Fibrin.** Insoluble in water; with difficulty soluble in dilute acids and alkalis, and in neutral saline solutions.

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* Lubavin's experiments seem also to show that casein, like vitellin or hæmoglobin, is a compound of an albuminous or proteid substance with a non-albuminous body.

rubbish-heaps of mines from which argentiferous galena and iron pyrites are obtained. Contains 30·47 p. c. SO^3, 46·50 Fe^2O^3, and 16·04 water, together with 1·86 As^2O^3, 2·40 SiO^2, 1·25 PbO, and 0·89 lime, clay, and manganese (Bergemann, *Jahresb.* 1867, p. 1005).

PATELLARIC ACID. $C^{17}H^{20}O^{10}$.—This acid, obtained some time ago by Knop, from the lichen *Parmelia scruposa* or *Patellaria scruposa*, has been further examined by Weigelt (*Zeitschr. f. Chem.* [2] v. 298). It does not appear to be identical with any of the known lichen acids. It unites easily with bases, and yields with cold baryta-water a salt having a transient blue colour. Boiling baryta-water decomposes it, forming carbonate and oxalate of barium, together with a barium salt of a new acid (*β patellaric acid*) possessing, to a certain extent, essentially different qualities. Patellaric acid forms two series of salts, in which 1 and 2 at. H are replaced by metals. The formation of the salt $C^{17}H^{18}(NH^4)^2O^{10}$ appears to require the aid of sunshine. Among the decomposition-products of the acid are carbonic acid, oxalic acid, and orcin. The lichen contains between 2 and 3 per cent. of patellaric acid. The acid is situated between the layers of the outer bark and the gonidia, where it was detected microscopically by the reaction with baryta-water.

PATSCHOULI. Volatile oil of patschouli gradually deposits a camphor or stearoptene, the formation of which may be accelerated by dehydrating the oil with calcium chloride. This camphor is homologous with that of Borneo, and has the composition $C^{15}H^{28}O$; vapour-density obs. = 8·00; calc. = 7·85. It melts at 54°–55°, boils at 296°, and has a sp. gr. of 1·051 at 4·5°. It is insoluble in water, easily soluble in alcohol and ether, and separates from these solutions by slow evaporation, sometimes in large and very well-defined hexagonal prisms terminated by six-sided pyramids. The alcoholic solution is lævogyrate, a solution of 1 grm. in 5·3 c. c. alcohol in a tube 0·05 met. long producing a deflection of 9·1°. The camphor distilled over zinc chloride yields a hydrocarbon, $C^{15}H^{26}$, which boils at 248°–252°, and appears to be converted into polymeric hydrocarbons at slightly higher temperatures. The oil from which the camphor has been deposited passes over almost entirely between 282° and 294°, has the same composition as the camphor, and yields the same hydrocarbon when treated with zinc chloride. It is also lævogyrate, but less so than the camphor, producing under the conditions above mentioned, a deflection of only 3° (H. Gal, *Compt. rend.* lxviii. 406).

PECTOLITE. The mineral from Niederkirchen, near Wolfstein in the Rheinpfalz, called *osmelite* by Breithaupt, appears, from a renewed examination by v. Kobell (*J. pr. Chem.* xcvii. 493; *Jahresb.* 1866, p. 935), to have the composition and all the properties of pectolite. It is intergrown with a brown friable mineral, very similar to it in structure, which appears to have been formed from it by the action of water and carbonic acid.

PECTOUS SUBSTANCES (iv. 363). On the preparation of pectin from turnips, see Stüde (*Ann. Ch. Pharm.* cxxxi. 244; *Jahresb.* 1864, p. 587).*

On the preparation of metapectic acid from horse-chestnut bark, see Rochleder (*Zeitschr. f. Chem.* [2] iv. 381). Metapectic acid heated with excess of potassium hydrate is resolved into formic and protocatechuic acids:

$$C^8H^{10}O^7 = CH^2O^2 + C^7H^6O^4 + H^2O.$$

The formation of pyropectic acid, $C^{14}H^{18}O^9$, from metapectic acid, by the action of heat, is represented by the equation: $2C^8H^{10}O^7 = C^{14}H^{18}O^9 + 2CO^2 + H^2O$ (Rochleder).

Scheibler (*Deut. chem. Ges. Ber.* 1868, pp. 58, 108; *Zeitschr. f. Chem.* iv. 433) prepares metapectic acid by heating turnip-pulp with milk of lime on the water-bath, decomposing the resulting calcium salt with ammonium carbonate, precipitating the ammoniacal solution with basic lead acetate, separating the acid by hydrogen sulphide (removing the last portions of lead, if necessary, by sulphuric acid), and decolorising it with animal charcoal free from lime. The acid thus prepared possesses all the properties of that described by Frémy (iv. 369), excepting that its alkali-metal salts are not precipitated by basic or neutral lead acetate in neutral solution, but only on addition of ammonia; and that, instead of being optically inactive, it exhibits a very strong lævogyration, 1 pt. of it being sufficient to neutralise the dextrogyrate power of 1⅓ pt. dextroglucose. This lævogyrate power is not altered by saturating or supersaturating the solution of the acid with alkalis or alkaline earths; but on boiling the solution with a strong acid, mineral or organic, it quickly diminishes, composition (C 51·8, H 6·9, N 12·8, O 26·8, S 1·7), and besides contains, or is associated with, a body resembling glycogen, and capable of conversion into a substance with many of the reactions of sugar.

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* See also vol. iv. p. 364, in which (line 9 from bottom) read 'turnips' instead of 'radishes.'

The relations of these various proteids may be tabulated thus:

Soluble in water:	
Aqueous solutions not coag. by boiling . .	PEPTONES.
Aq. sol. coag. by boiling	ALBUMINS.
Insoluble in water:	
Soluble in NaCl sol. 1 p. c.	GLOBULINS.
Insoluble „ „	
Soluble in HCl, 1 p. c. in the cold:	
Soluble in hot spirit	ALKALI-ALBUMIN.
Insoluble „	ACID-ALBUMIN.
Insol. in HCl, ·1 in the cold:	
Sol. in HCl, ·1 p. c. at 60° . .	FIBRIN.
Insoluble in HCl, ·1 p. c. at 60°; sol. in strong acids:	
Sol. in gastric juice . . .	COAGULATED ALBUMIN.
Insol. in gastric juice . .	AMYLOID.

The above method of solubilities is the only means at our command for distinguishing them. From their elementary composition we learn nothing, as may be gathered from the following table:

	C	H	N	O	S
Fibrin . . .	52·6	7·0	17·4	21·8	1·2
Syntonin . .	54·1	7·3	16·1	21·5	1·1
Peptone . . .	50·87	7·03	16·34	24·12	1·64
Albumin . .	51·37	7·13	19·00	23·12	2·12
Lardacein . .	53·6	7·0	15·0	23·1	1·3
In general from .	52·7	6·9	15·4	20·9	·8
„ to . .	54·5	7·3	16·15	23·5	2·0

Many circumstances seem to point to the conclusion that undigested proteids are converted during digestion into peptones, by a process of cleavage, with assumption of water, analogous to that by which starch is converted into grape-sugar. And the fact that peptones of some kind or other are produced, not only by digestion, but also by ordinary chemical means, as the action of acids, &c., seems to point the same way. The various decompositions of peptone (and of the other proteids), especially that by pancreatic juice, indicate moreover that leucine and tyrosine are distinct elements in its structure; but other products appear to be invariably formed at the same time. Further than this we are at present unable to go.

A distinction may be drawn between 'natural' proteids, such as albumins, globulins, fibrin, and modified ones, such as acid- and alkali-albumin, which are produced by some actions (as of acid, &c.) on the former, either within or without the body. The great feature of all them is their instability. The most stable are the peptones and coagulated albumin, next come fibrin and albumin, then acid- and alkali-albumin, and, least stable of all, the globulins. So incessant are the changes they undergo, that it may be doubted whether they are fixed chemical compounds in the ordinary sense of that term.

For further details respecting proteids, see *Gmelin's Handbook*, xviii. 252–469.

M. F.

PROTOCATECHUIC ACID. $C^7H^6O^4$.—The formation of this acid, together with phloroglucin, by the action of melting potash on a variety of organic substances, is noticed under PHLOROGLUCIN (p. 928). It is also formed, together with acetic acid, by fusing caffeic acid with potash (Hlasiwetz, *Ann. Ch. Pharm.* cxlii. 219); by similar treatment of cinchona-red (Rembold, *ibid.* cxliii. 273); together with resorcin and volatile fatty acids, by fusing asafœtida with potash (Hlasiwetz a. Barth, *ibid.* cxxxviii. 61); and, together with pyrocatechin, by fusing sulphanisic acid with potash (Malin, *Ann. Ch. Pharm.* clii. 109).

A mixture of monobasic barium protocatechuate, $(C^7H^5O^4)^2Ba$, with saturated baryta-water, deposits after a while warty crusts of a tribasic salt, $(C^7H^3O^4)^2Ba^3$ (at 130°), analogous to the triplumbic salt obtained by Strecker (iv. 739).

Bromoprotocatechuic acid, $C^7H^5BrO^4$, obtained by triturating the acid with bromine, and warming the product over the water-bath, crystallises from hot water in dense anhydrous rhombic needles, and when heated with a concentrated solution of 4 pts. potassium hydrate to a pasty consistence, acidulated with sulphuric acid, and exhausted with ether, yields an acid crystallising in rhombic needles, and approximating in composition to gallic acid, $C^7H^6O^5.H^2O$. Protocatechuic acid is probably identical with carbohydroquinonic acid, inasmuch as these two acids agree in their reactions, melting point, and crystalline form, and when heated with hydriodic acid to 140°, yield, together with carbon dioxide, a mixture of hydroquinone and pyrocatechin (Barth, *Ann. Ch. Pharm.* cxlii. 246).

PROTOCATECHUIC ALDEHYDE, $C^7H^6O^3$, isomeric with oxybenzoic acid, is produced by heating dichloropiperonal with water (p. 948):

$$C^8H^4Cl^2O^3 + 2H^2O = CO^2 + 2HCl + C^7H^6O^3.$$

It is easily soluble in water, and crystallises from the concentrated solution mostly in concentric groups of flat crystals, which are best purified by recrystallisation from toluene. It melts and becomes dark-coloured at 150°, and decomposes at a higher temperature with separation of carbon. The aqueous solution mixed with ferric chloride acquires a very deep and pure green colour, changing to red on addition of a drop of solution of sodium carbonate. A similar reaction is exhibited by protocatechuic acid, but the green is not pure, inclining more to blue. The aldehyde is oxidised to protocatechuic acid by fusion with potash, also by permanganates. From ammoniacal silver-solution it throws down a silver speculum. It appears to unite with alkaline bisulphites, but without forming crystalline compounds (Remsen & Fittig, *Zeitschr. f. Chem.* [2] vii. 100).

PSEUDO-ALCOHOLS. See ALCOHOLS (p. 65).

PSEUDOCUMENE. *Trimethyl-benzene.*—See BENZENE, HOMOLOGUES OF (p. 296).

PSEUDOCURCUMIN. See CURCUMIN (p. 517).

PSEUDOMORPHINE. $C^{17}H^{19}NO^4$ (O. Hesse, *Ann. Ch. Pharm.* cxli. 87).—This base, first noticed by Pelletier (iii. 1051), may be obtained in the preparation of morphine by Gregory's process, in the following manner. When the purified mixture of the hydrochlorides of morphine, codeine, &c., is mixed with a slight excess of ammonia, only the morphine is precipitated, and the filtrate, slightly supersaturated with hydrochloric acid, freed from alcohol, and somewhat decolorised by animal charcoal, yields, on neutralisation with dilute ammonia, a bulky precipitate, chiefly consisting of pseudomorphine. On washing this precipitate with water, dissolving it in acetic acid, and mixing the filtered solution with such a quantity of dilute ammonia that the supernatant liquid shall just slightly redden blue litmus-paper, only the pseudomorphine is precipitated, and may be purified by combining it with hydrochloric acid, and decomposing the recrystallised salt in hot aqueous solution with ammonia.

Pseudomorphine thus prepared is a finely crystalline white precipitate, having a silky lustre, and drying up to a dull white mass; when separated from a cold solution, it is gelatinous, and after prolonged drying, translucent and horny. It is insoluble in water, alcohol, ether, chloroform, carbon bisulphide, dilute sulphuric acid, and sodium carbonate, but dissolves easily in caustic alkalis and milk of lime. Aqueous ammonia dissolves it sparingly, but alcoholic ammonia dissolves it very easily when recently precipitated. Its solution in strong sulphuric acid is olive-green; the nitric acid solution has a deep orange-red colour, changing to yellow; the solution in ferric chloride is blue. The base and its salts are tasteless. The base dried at 120° has the composition $C^{17}H^{19}NO^4$; in the air-dried state it appears to contain 1 mol. water (5·6 p. c.). It is perhaps identical with Schutzenberger's oxymorphine (p. 841). The *hydrochloride*, $C^{17}H^{19}NO^4.HCl + H^2O$, is a white crystalline powder, insoluble in alcohol and dilute sulphuric acid, soluble in 70 pts. water at 20°; the *platinochloride*, $2(C^{17}H^{19}NO^4.HCl).PtCl^4$, is a yellow amorphous precipitate. The *sulphate*, $2C^{17}H^{19}NO^4.H^2SO^4 + 6H^2O$, precipitated on mixing the hydrochloride with an equivalent quantity of sodium sulphate in slightly acidulated solution, forms small white laminæ very much like gypsum. The *oxalate*, $2C^{17}H^{19}NO^4.C^2H^2O^4 + 6H^2O$, is a white precipitate composed of prismatic crystals; the *tartrate* forms sparingly soluble prisms; the *nitrate* shining laminæ; the *chromate* a yellow crystalline precipitate; the *hydriodide* pale yellow prisms; the *aurochloride* a yellow amorphous precipitate; the *mercurochloride* a precipitate composed of colourless prisms.

PSEUDONEPHRITE. A calcio-aluminic silicate resembling nephrite, from Easton, described by A. Emmerling (*Jahrb. Min.* 1866, p. 558; *Jahresb.* 1866, p. 939).

PSEUDOSULPHOCYANATES. See SULPHOCYANATES.

PTEROLITE. A mineral occurring in the Brevig Sound in Norway, together with pitch-black mica, astrophyllite, wöhlerite, and ægirin. It is massive and composed of numerous lamellæ, grouped like the beard of a feather and partly curved. Hardness = 2·5 to 3. Sp. gr. 3·063 to 3·666. Colour olive-green and liver-brown; lustre nacreous. Translucent only at the edges. An analysis by R. Müller gave

SiO^2	Al^2O^3	CaO	MgO	K^2O	Na^2O	FeO	Fe^2O^3	H^2O	
39·38	6·65	5·47	0·56	7·86	2·81	16·43	19·89	1·39	= 100·44

(Breithaupt, *Jahrb. Min.* 1865, p. 858; *Jahresb.* 1865, p. 887).

PURPURIN. According to the recent investigations of Strecker (*Zeitschr. f. Chem.* [2] iv. 265), and of Graebe a. Liebermann (*ibid.* 503), this substance has the composition of oxyalizarin, $C^{14}H^8O^5$. For Bolley's experiments on the composition of purpurin and other madder colours, see *Dingl. pol. J.* clxxxii. 351; *Jahresb.* 1866, p. 643. For E. Kopp's method of preparing purpurin, &c., from madder, see *Bull. Soc. industr. de Mulhouse*, xxxvii. 437; *Jahresb.* 1867, p. 955.

PURPUROGALLIN. $C^{20}H^{16}O^9$ (A. Girard, *Compt. rend.* lxix. 865; *Zeitschr. f. Chem.* [2] vi. 86).—A red colouring matter produced by oxidation of pyrogallic acid with silver nitrate in alcoholic solution, or more conveniently with permanganic acid. 60 grams of potassium permanganate are dissolved in a litre of water mixed with 55 grams of hydrogen sulphate, and this solution is gradually poured into a strong aqueous solution containing 40 grams of pyrogallic acid. Purpurogallin then separates in orange-red flocks, which may be purified by washing with a little water and crystallisation from alcohol, or by sublimation. It sublimes at about 200° in garnet-red needles, having a finer colour and stronger lustre than alizarin. It dissolves sparingly in water, more easily in alcohol, also in ether and in benzol, forming yellow solutions. Sulphuric acid dissolves it, forming a compound which crystallises in crimson needles decomposed by water. Most other acids dissolve it without alteration. Nitric acid attacks it energetically; the very concentrated acid may even set it on fire; ordinary nitric acid converts it into picric acid. Alkalis impart to the solutions of pyrogallin a transient blue colour; aluminium sulphate, on addition of ammonia, throws down a violet-blue lake, which gradually turns brown. Lead acetate forms a red-brown precipitate. Silver nitrate colours the solutions violet-blue, then brown, with separation of metallic silver. Auric chloride forms a bright carmine-red solution, which however also turns brown and deposits metallic gold. Purpurogallin dyes mordanted fabrics quickly and completely, but the colours are not very good.

PYRIDINE. C^5H^5N.—According to Chapman a. Smith (*Ann. Ch. Pharm. Suppl.* vi. 329; *Jahresb.* 1868, 682), this base is formed by dehydration of amyl nitrite, *e.g.* when that compound is heated with phosphoric anhydride, $C^5H^{11}NO^2 - 3H^2O = C^5H^5N$.

Dipyridine. $C^{10}H^{10}N^2$ (Anderson, *Chem. Soc. J.* [2] vii. 406).—This base, polymeric with pyridine, is formed, together with other products, by the action of sodium on pyridine. When dry pyridine is heated to its boiling point with small pieces of sodium amounting to about one-fifth of its weight, in a flask furnished with a long condensing-tube, the whole is gradually converted into a dark brown or black mass, which solidifies on cooling to a hard brittle resin; and on separating this resin as completely as possible from unaltered sodium, and throwing it by small pieces into water, it is slowly converted into a thick brown oil, which collects at the bottom of the vessel, and when washed with water, dried with calcium chloride, and distilled in a current of hydrogen, yields at first a light oil consisting of several bases, then a thick heavy oil which deposits crystals of dipyridine. On redistilling this product, dipyridine crystallises in the neck of the retort, and the fluid portions of the distillate yield a further quantity of it when cooled by a freezing mixture. The formation of dipyridine by the action of sodium on pyridine takes place also in the cold. In this case, the sodium becomes covered, in the course of a few days, with a black brittle crust, which when washed with pyridine to remove an oil formed at the same time, then detached as completely as possible from the sodium, and thrown into water, yields a dark grey powder, which falls to the bottom. This powder washed till free from soda, and then spread out in contact with the air, is entirely converted into a snow-white mass of interlaced acicular crystals, consisting of dipyridine.

Dipyridine melts at 108°; solidifies to a crystalline mass on cooling; volatilises slowly at 100°; and sublimes unchanged at a high temperature, in long needle-shaped

PHENOL. $C^6H^6O = C^6H^5OH$. *Phenyl Hydrate. Phenyl Alcohol.*—This compound is formed: 1. By heating anisol with concentrated hydriodic or hydrochloric acid to 130°–140° (Graebe, *Ann. Ch. Pharm.* cxxxix. 149):

$$C^6H^5OCH^3 + HI = CH^3I + C^6H^5OH.$$

2. By boiling the sulphate, nitrate, or hydrobromide of diazobenzene with water (Griess, *ibid.* cxxxvii. 39):

$$C^6H^4N^2.SO^4H^2 + H^2O = SO^4H^2 + N^2 + C^6H^6O.$$

3. By fusing potassium phenylsulphite with excess of potash (Wurtz, *Bull. Soc. Chim.* [2] viii. 197):

$$C^6H^5.SO^3K + KOH = SO^3K^2 + C^6H^5OH.$$

4. By heating acetylene with fuming sulphuric acid, whereby it is converted into the acid $C^2H^2SO^3$, and fusing the potassium salt of this acid with potash. The acetylene is then separated and polymerised, and the polymeric compound takes up oxygen, $3C^2H^2 + O = C^6H^6O$ (Berthelot, *Compt. rend.* lxviii. 539).

The phenol obtained by distilling oxybenzoic acid with lime (iv. 205) is identical with that produced in like manner from parabenzoic and salicylic acids, and with that obtained from coal-tar (Rosenthal, *Zeitschr. f. Chem.* [2] v. 627).

Preparation.—The following method of obtaining pure phenol from coal-tar is given by Hugo Müller (*Zeitschr. f. Chem.* [2] i. 270). The aqueous solution obtained by treating coal-tar with caustic soda or milk of lime, or a mixture of the two—which contains, besides phenol, certain easily oxidisable substances, and a not inconsiderable quantity of naphthalene—is diluted with water as long as naphthalene is thereby separated, and the liquid, which soon turns dark brown, is exposed to the air in shallow vessels for several days and frequently stirred. The brown solution is then filtered, the quantity of phenol contained in a given quantity of it is determined; and the quantity of acid required to precipitate the entire amount is calculated therefrom. If now $\frac{1}{6}$ to $\frac{1}{8}$ of this quantity of acid be added to the liquid with constant stirring, the resinous substances altered by the action of the air are first precipitated, together with larger or smaller quantities of cresol and xylol. A further addition of acid precipitates chiefly cresol, and after a few trials it is generally possible so to adjust the quantity of acid that the third and last precipitation shall yield nearly pure phenol, which crystallises after a single distillation. As even a small quantity of water prevents the crystallisation of phenol, it is necessary to remove this water completely by heating the phenol nearly to the boiling point, while a stream of dry air is passed over it. The crystallisation may be accelerated by cooling, or by the introduction of a small quantity of crystallised phenol. Crude phenol, such as is obtained from tar-refineries, may be conveniently purified by treating it several times in succession with soda-ley. The first extracts contain the purer product: the precipitation of the phenol must however be preceded by dilution with water and exposure to the air. A perfectly pure product, remaining colourless when preserved, is obtained only when the substances which turn brown by oxidation have been completely removed by exposure to the air. Phenol commonly contains a small quantity of a very disagreeably smelling sulphur-compound (phenyl sulphide), which may be removed by distillation over a small quantity of lead oxide.

For the preparation of crystallised phenol, Bickerdike (*Chem. News*, xvi. 188) recommends that the commercial product purified by one rectification be dehydrated with 1 or 2 p. c. of anhydrous cupric sulphate. The distillate solidifies for the most part at 16°, especially in contact with solid phenol.

Reactions.—1. An alcoholic solution of phenol is turned brown by an alcoholic solution of *ferric chloride*; wood-tar creosote similarly treated yields a solution of a fine emerald-green colour (Frisch, *J. pr. Chem.* c. 223:—Gorup-Besanez, *Ann. Ch. Pharm.* cxliii. 129).—2. When a few sticks of potash are immersed in a solution of phenol in chloroform, the potash becomes covered with a rose-coloured layer which gradually dissolves, the liquid becoming very hot and ultimately brown and viscid. The first product is a brown amorphous mass, soluble in alkalis, reprecipitated by acids, and apparently consisting of two substances, one of which dissolves very easily in alkaline carbonates, less easily in strong sulphuric acid; this latter solution gives with water, a precipitate exhibiting with alkalis the reactions of rosolic acid. The other substance is less soluble in alkalis, but dissolves very easily in strong sulphuric acid, and is not reprecipitated by water. If carbon tetrachloride be used as the solvent instead of chloroform, no reaction takes place in the cold, but at 180° the liquid assumes the colour of rosolic acid. When wood-tar creosote is treated in the same manner, a very similar reaction takes place, but the product is altogether

34·56 H^2O, and 7·24 CO^2 (= 99·76). The carbon dioxide must be regarded as an accidental admixture. The mineral is named pyroaurite on account of its property of acquiring a gold-colour in the fire (Igelström, *Jahresb.* 1867, p. 981).

PYROCATECHIN. The meta- modification of oxyphenol, $C^6H^6O^2$, produced: α. By the action of melting potash on meta-iodophenol. Ordinary iodophenol (produced by treating phenol with iodine and iodic acid) yields a mixture of hydroquinone and pyrocatechin (Körner, *Bull. Acad. Belg.* [2] xxiv. 166).—β. By the action of hydriodic acid on guajacol: $C^7H^8O^2 + HI = CH^3I + C^6H^6O^2$ (Gorup-Besanez, *Jahresb.* 1867, p. 688).—γ. By the dry distillation of protocatechuic acid, and, together with hydroquinone, benzoic acid, benzene, and phenol, by the dry distillation of quinic acid (Hlasiwetz a. Barth, *ibid.* 1864, p. 398, 405). It is also one of the products of the distillation of benzoïn (Hlasiwetz a. Barth, *Jahresb.* 1866, p. 574).

PYROGALLIC ACID. According to J. Personne (*Zeitschr. f. Chem.* [2] v. 728), this acid acts poisonously on the animal organism, in the same manner as phosphorus, namely by abstracting the oxygen of the blood.

Pyrogallic acid heated with picric acid and a little water unites with the picric acid, forming a compound which crystallises in large laminæ, and blackens slightly on exposure to the air (De Luynes, *ibid.* iv. 703). By oxidation with silver nitrate, permanganic acid, and other reagents, it yields purpurogallin (p. 977).

PYRO-ISOMALIC ACID. $C^6H^8O^5$.—An acid produced by the action of heat on isomalic acid (p. 753).

PYRO-ITARACEMIC ACID. $C^4H^6O^3$.—An acid formed by the dry distillation of itatartaric acid (p. 762).

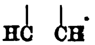
PYROMUCIC ACID. $C^5H^4O^3$ (Limpricht, *Zeitschr. f. Chem.* [2] v. 599).—For the preparation of this acid, Limpricht gives the preference to Ulrich's method of treating furfurol with alcoholic potash (iv. 763); the product amounts to 33 p. c. of the furfurol employed.

Pyromucic acid in aqueous solution is decomposed by bromine, yielding the compound $C^4H^4O^2$; thus:

$$C^5H^4O^3 + H^2O + Br^2 = CO^2 + 2HBr + C^4H^4O^2.$$

This acid is however immediately converted into the brominated acid, $C^4H^3BrO^2$, which distils over and solidifies in white feathery crystals, convertible by sodium-amalgam into a transparent liquid of low boiling point, having the composition $C^4H^4O^2$. The compound $C^4H^3BrO^2$ is converted by further action of the bromine into $C^4H^2Br^2O^2$, which when treated with silver oxide, or when its aqueous solution is evaporated, exchanges its bromine for hydroxyl, and is converted into maleic or fumaric acid, $C^4H^4O^4$. The dibrominated acid, $C^4H^2Br^2O^2$, is still further converted by the free bromine into $C^4HBr^3O^2$, which also, when the solution is evaporated, exchanges 1 at. bromine for hydroxyl, and is converted into mucobromic acid, $C^4H^2Br^2O^3$ (iv. 763).

Limpricht regards the compounds of the pyromucic group as derivatives of the hydrocarbon



$$\begin{array}{l} HC{=}CH \\ \,|\qquad | \\ HC\quad CH \end{array}.$$

PYROPHOSPHAMIC ACIDS. See PHOSPHAMIC ACIDS (p. 930).

PYROPHOSPHATES. See PHOSPHORIC ACIDS (p. 940).

PYRORACEMIC ACID. $C^3H^4O^3$.—This acid is formed by gradually heating racemic acid in sealed tubes to 180° with hydrochloric acid (Geuther a. Riemann, *Zeitschr. f. Chem.* [2] v. 318). According to Wichelhaus (*Jahresb.* 1867, p. 403; further, *Ann. Ch. Pharm.* clii. 260), it does not exhibit the characters of an oxyacid. On mixing it with excess of phosphorus pentachloride, and heating the mixture to boiling after phosphorus oxychloride has been formed, then pouring it when cold into water, the water takes up ordinary pyroracemic acid (altered by boiling), which may be extracted from it by ether. Hence it appears that pyroracemic acid does not contain any alcoholic hydrogen. Wichelhaus represents it by the constitutional formula $CH^3—CO—CO^2H$, regarding it as homologous to carbacetylic acid and glyoxylic acid, ($C^2H^2O^3$).

Pyroracemic is not reduced by hydriodic acid or attacked by acetyl chloride at the boiling heat. Pyroracemates subjected to dry distillation in contact with acetates yield acetone and pyrotartaric acid (Wichelhaus, *Zeitschr. f. Chem.* [2] v. 254).

Dry pyroracemic acid heated in a sealed tube with 1 mol. bromine is converted into dibromolactic acid, $CH^2Br—CBrOH—CO^2H$ (Wislicenus, p. 771).

Bromopyroracemic acids (mono- and di-) are formed by heating pyroracemic acid to 100° in a sealed tube with 1 or 2 mol. bromine and water. The *dibromo-pyroracemic acid* is more easily otained pure than the monobrominated acid, and may be extracted from the water by ether. It crystallises from aqueous solution in large monoclinic tables, which contain $C^3H^2Br^2O^3 + H^2O$, and give off their 1 mol. water even on exposure to the air, more quickly in a vacuum. The effloresced acid crystallises from anhydrous solvents in long needles melting at 89°–91°. If the acid during its preparation be exposed for a long time to a high temperature, it is decomposed, with formation of pentabromacetone, C^3HBr^5O:

$$CHBr^2—CO—CO^2H + 3HBr = 2H^2O + CHBr^2—CO—CBr^3.$$

Dibromopyroracemic acid is decomposed by silver oxide, giving up all its bromine and being converted in the cold, chiefly into mesoxalic acid, $C^3H^2O^5$; at a gentle heat silver is separated, and carbon dioxide is evolved. It is carbonised by alcoholic ammonia, but aqueous ammonia converts it into *imido-pyroracemic acid*, CH(NH)—CO—CO²H. This compound possesses but slightly acid properties, and crystallises indistinctly; it unites directly with nitric acid, and gives with silver nitrate a white curdy precipitate, containing $C^3HAg(NH)O^3 . AgNO^3$. *Monobromo-pyroracemic acid* has been obtained only as a syrupy liquid, which when treated with silver oxide, gives off carbon dioxide, as soon as the liquid becomes neutral, even at low temperatures. At a gentle heat silver acetate is produced (Wichelhaus, *loc. cit.*)

PYROTARTARIC ACID, $C^5H^8O^4$, is produced by heating pulverised tartaric acid to 180° in sealed tubes with hydrochloric acid (Geuther a. Riemann, *Zeitschr. Chem.* [2] v. 318); also, as above observed, by heating pyroracemates with acetic (Wichelhaus); also, together with several other products, by fusing gamboge with potash (Hlasiwetz a. Barth, p. 628).

The *chloro-*, *bromo-*, and *iodo- derivatives* of pyrotartaric acid are formed, not from that acid itself, but by direct addition of Br^2, Cl^2, I^2, or of HBr, HCl, HI to the pyrocitric acids, $C^5H^6O^4$, and they exhibit different modifications, according as they are formed from citraconic, itaconic, or mesaconic acid. (See ACIDS, ORGANIC, p. 49.) The dibromo-compounds, obtained by addition of bromine to these acids, were discovered by Kekulé, and are described in vol. iv. pp. 773, 774. The mono-chlorinated, monobrominated, and monoiodated derivatives have been studied by Swarts (*Bull. Acad. Belg.* [2] xvii. xix.; *Instit.* 1865, p. 23; 1866, pp. 323, 358; *Jahresb.* 1865, p. 392; 1866, p. 404); they are formed by addition of HCl, HBr, and HI, to itaconic, citraconic, and mesaconic acid respectively.

Citramonochloropyrotartaric acid, $C^5H^7ClO^4$, formed by heating citraconic anhydride to 120° for two or three hours with an equal volume of strong hydrochloric acid, crystallises from ether in nacreous laminæ unctuous to the touch. *Both in the* dry state and in solution it is decomposed by the slightest elevation of temperature into hydrochloric and mesaconic acids. Heated with bases, it is resolved, like citra-dibromopyrotartaric acid, into carbon dioxide and crotonic acid:

$$C^5H^7ClO^4 = C^4H^6O^2 + HCl + CO^2.$$

In cold water it dissolves without decomposition, and the solution is not precipitated by silver nitrate; but on gently heating it, a precipitate of silver chloride is formed.

Itamonochloropyrotartaric acid is formed by heating pulverised itaconic acid to about 130° for three hours with 2 pts. of very strong hydrochloric acid, washing the product with cold water, and recrystallising from water or alcohol. It forms white lustreless nodules or crystals, like those of pyrotartaric acid, inodorous, and having an agreeable sour taste. It melts at 140°–145°, remaining liquid for a long time, and boils at 225°–230°, forming water, hydrochloric acid, and an oily anhydride which crystallises after a while, and is reconverted into the original acid. Heated to 150° in a stream of dry air, it gives off water, and leaves the anhydride, which, however, cannot be obtained pure, in consequence of simultaneous loss of hydrochloric acid. Hot water converts it into itamalic acid (p. 761):

$$C^5H^7ClO^4 + H^2O = HCl + C^5H^8O^5.$$

The same decomposition is produced by strong bases; but the solution saturated with ammonia deposits sal-ammoniac on evaporation, and the mother-liquor contains mesaconic acid. Treated with silver oxide, it yields, together with silver chloride, the silver salt of paraconic acid, isomeric with itaconic acid, but monobasic (p. 760). *Ethylic itachloropyrotartrate*, $C^5H^5Cl(C^2H^5)^2O^4$, is obtained, by saturating the alcoholic solution of the acid with hydrochloric acid gas, and rectifying the liquid precipitated by water, as a colourless bitter liquid, which boils at 250°–252°, with formation of a small quantity of hydrochloric acid.

Mesamonochloropyrotartaric acid is formed by repeatedly heating mesaconic acid to 160° with very strong hydrochloric acid. The solution of the product deposits on evaporation, first lustreless nodules of unaltered mesaconic acid, then small shining crystals of the much more soluble chlorinated acid. The latter melts at 129°–130°, and is resolved by boiling with water into hydrochloric and mesaconic acids. It is converted by bases into crotonic acid.

Itadichloropyrotartaric acid, $C^5H^6Cl^2O^4$, formed by addition of chlorine to itaconic acid, is very soluble, forms large crystals, and is decomposed by boiling its solution.

Itamonobromopyrotartaric acid, $C^5H^7BrO^4$, is prepared, like the chlorinated acid, by heating itaconic acid for half an hour to 160° with concentrated hydrobromic acid; also, though less advantageously, by the action of bromine on pyrotartaric acid at 120°; also by the action of fuming hydrobromic acid on itamalic acid: $C^5H^8O^5 + HBr = H^2O + C^5H^7BrO^4$. It melts at 130°–134°, remaining liquid for a long time, and boils without decomposition at about 250°. It is less easily decomposed by boiling water than the chlorinated acids, and reacts exactly like the latter with bases. *Ethyl itabromopyrotartrate* is obtained by heating the acid with alcohol to 110°; the product precipitated by water boils, with partial decomposition, at 270°–275°.

Itamoniodopyrotartaric acid, $C^5H^7IO^4$, is prepared by heating itaconic acid somewhat in excess with hydriodic acid to 150° in an atmosphere of carbon dioxide: if an excess of hydriodic acid be used, pyrotartaric acid will be likewise formed. The liquid purified from free iodine by treatment with mercury, deposits, on evaporation over sulphuric acid, dull nodular groups of crystals of the iodated acid (mixed with a little itaconic acid), which become colourless by repeated crystallisation from water. They melt at 135°, and decompose at 185°, with evolution of iodine. Boiling water produces only slow decomposition. The acid heated with hydriodic acid is reduced to pyrotartaric acid, with separation of iodine. Heated with alcohol containing hydrochloric acid, it yields ethylic itamono-iodopyrotartrate.

Citra-iodopyrotartaric acid cannot be isolated. When citraconic anhydride is heated with fuming hydriodic acid, a brown crystalline mass separates on cooling, which when submitted to purification, is resolved into hydriodic and mesaconic acids. Since however pyrotartaric acid is obtained by continued heating of citraconic anhydride with fuming hydriodic acid, it may be supposed that citra-iodopyrotartaric acid is formed as an intermediate product.

PYROTRITARTARIC ACID. $C^7H^8O^3$ (Wislicenus a. Stadnicki, *Ann. Ch. Pharm.* cxlvi. 306).—A crystalline acid formed, together with pyrotartaric acid, by the dry distillation of tartaric acid: $3C^4H^6O^6 = C^7H^8O^3 + 5CO^2 + 5H^2O$. It is obtained most abundantly by somewhat rapid distillation, but always in very small quantity, not exceeding 0·02 p. c. To separate it, the products distilling between 120° and 180° are subjected to repeated fractional distillation. Nearly pure pyrotartaric acid is then obtained between 160° and 170°, and between 180° and 210°, a series of gradually diminishing fractions, which as they cool partly deposit the pyrotritartaric acid in needle-shaped crystals. On dissolving these products in boiling water, whereby the admixed pyrotartaric anhydride is converted into pyrotartaric acid, and filtering at the boiling heat through wetted filters, the pyrotritartaric acid separates on cooling in yellowish needles, which may be purified by recrystallisation from boiling water with addition of animal charcoal. Pyrotartaric acid crystallises from the mother-liquors.

Pyrotritartaric acid forms colourless shining needles, soluble in about 400 pts. of boiling water, less soluble in cold water, easily soluble in alcohol and ether, and crystallising from the latter in short thick prisms. The solutions have a decided acid reaction. The acid melts at 134·5°, sublimes even below this temperature, in small needles, and easily passes over with vapour of water. The pyrotritartrates of the alkali-metals are easily soluble in water; probably also those of the alkaline-earth metals. The lead and silver salts are white precipitates, insoluble in water, and becoming crystalline when immersed therein.

The acid treated with phosphorus pentachloride is converted into the chloride $C^7H^7O^2Cl$, which, however, is immediately reconverted by water into pyrotritartaric acid. Wislicenus and Stadnicki regard this acid as a ketonic acid, $C^5H^7—CO—COOH$, although no hydrogen can be introduced into it by the action of sodium-amalgam. From its properties it might rather be supposed to belong to the aromatic group.

PYRRENE. See AUGITE.

PYRROL. C^4H^5N. This compound may be prepared by heating ammonium mucate with glycerin in a retort to 180°–200°, the resolution of the ammonium salt into pyrrol and ammonium carbonate then proceeding more regularly than by distillation. Silver oxide is reduced by pyrrol, with formation of a sublimable, easily soluble acid, which forms sparingly soluble compounds with silver and lead (Goldschmidt, *Zeitschr. f. Chem.* [2] iii. 280). The body thus formed reduces silver oxide almost as strongly as pyrrol itself: hence it is probable that the oxidation of pyrrol by silver oxide might be carried much further (Lubavin).

Sodium acts but slightly on pyrrol; but *potassium* acts very strongly, with great rise of temperature and evolution of gas, forming a thick, nearly colourless liquid which solidifies in the crystalline form on cooling, and probably consists of potassium-pyrrol, C^4H^4KN, inasmuch as, when treated with water, it yields unaltered pyrrol, and is converted by ethyl iodide into ethyl-pyrrol. The latter may be prepared by gradually adding 1 at. potassium and 1 mol. pyrrol to a mixture of pyrrol with 5 to 7 parts of ethyl iodide in a flask with upright condenser, assisting the action by a gentle heat, afterwards removing the excess of ethyl iodide by distillation at a water-bath, and distilling in an oil-bath. The resulting liquid subjected to fractional distillation yields ethyl-pyrrol between 155° and 175°. *Ethyl-pyrrol* is a colourless liquid, soon however turning yellow and red. It has a peculiar turpentine-like odour quite different from the ethereal odour of pyrrol. It is not perceptibly soluble in water, but floats upon it as an oil; becomes resinised by contact with air or by heating. It dissolves in hydrochloric acid, with copious evolution of white fumes, forming a dark red liquid, which does not deposit any solid substance on boiling, whereas pyrrol when heated with hydrochloric acid, becomes quite solid, from formation of pyrrol-red. Potash added to the solution boiled with hydrochloric acid, throws down an amorphous substance. The vapours of ethyl-pyrrol colour a deal-shaving moistened with hydrochloric acid red, just like pyrrol itself (Lubavin, *Zeitschr. f. Chem.* [2] v. 3[illegible]

Q

QUERCITRIN and **QUERCETIN.** Rochleder a. Kawalier have obtained quercitrin from the fully-developed leaves of the horse-chestnut, by fractionally precipitating the extract with basic lead acetate. Separated from the lead salt and dried at 100° in a vacuum, it gave by analysis numbers agreeing with the formula $C^{33}H^{30}O^{17}$, with 1, 2, 2½, and 3 mol. H^2O. The *quercetin* produced from it was composed of $C^{27}H^{18}O^{12} + H^2O$ (*Wien. Akad. Ber.* lv. [2] 46; *Jahresb.* 1867, p. 731). According to Rochleder (*loc. cit.* p. 211), the yellow colouring matter of the stem-bark of the apple-tree consists of hydrated quercetin having the same composition. Gintl (*Zeitschr. f. Chem.* [2] iv. 732) has found quercetin in the leaves of the ash-tree gathered towards the end of spring.

QUINIC ACID. $C^7H^{12}O^6$. This acid occurs, together with rubichloric acid and a small quantity of citric acid, in the herb of *Galium Mollugo* (F. Oehren, *Zeitschr. f. Chem.* [v] iii. 28).

Quinic acid treated with 5 mol. phosphorus pentachloride yields chlorobenzoyl chloride, together with phosphorus oxychloride and hydrochloric acid:

$$C^7H^{12}O^6 + 5PCl^5 = C^7H^4Cl^2O + 5POCl^3 + 8HCl.$$

By fusion with 4 pts. potassium-hydrate it is converted into carbohydroquinonic acid:

$$C^7H^{12}O^6 = C^7H^6O^4 + H^2 + 2H^2O$$

(Graebe, *Ann. Ch. Pharm.* cxxxviii. 197).

QUINIDINE. $C^{20}H^{24}N^2O^2$.—This base, isomeric with quinine, is, according to De Vrij (*Pharm. J. Trans.* xvi. 401), identical with the base first described in 1833 by Henry a. Delondre (*J. Pharm.* [2] xix. 623) as crystallised quinine-hydrate, and with the β-quinine obtained by Van Heijningen (*Jahresb.* 1849, p. 371) from commercial quinoïdine (v. 26).

F. Koch, on the other hand (*N. Jahrb. Pharm.* xxii. 240; *Jahresb.* 1864, p. 444), regards the base usually called quinidine as distinct from β-quinine, the latter according to his observations, occurring in all cinchona-barks, especially in Pitayo bark, the former in Carthagena, less frequently in Pitayo, never in Calisaya bark; but the differences do not appear to be very well made out.

needles. The *ferric salt*, obtained in like manner, crystallises in green laminæ moderately soluble in water. The *nickel salt*, $[C^6H^3(NO^2)^2O]^2Ni + 8H^2O$, forms green needles. The *manganous salt*, $[C^6H^3(NO^2)^2O]^2Mn + 5H^2O$, crystallises in tufts of rose-coloured easily soluble needles. The *quinine salt*, $C^6H^4(NO^2)^2O . C^{20}H^{24}N^2O^2 + 3H^2O$, is insoluble in ether, nearly insoluble in water, slightly soluble in alcohol, and crystallises from the latter in tufts of long orange-coloured needles, or from water in light yellow laminar masses. The *ethylic ether* (dinitrophenetol), $C^6H^3(NO^2)^2O . C^2H^5$, formed by heating the silver salt with ethyl iodide, crystallises from alcohol in nearly colourless needles blackened by light (compare iv. 399). The *methylic ether* (dinitranisol), $C^6H^3(NO^2)^2O.CH^3$, forms long very slender needles; the *amylic ether* is a heavy colourless oil. *Urea dinitrophenate* forms indistinctly crystalline masses. *Naphthalene dinitrophenate*, $C^6H^4(NO^2)^2O . C^{10}H^8$, crystallises from a solution of the two bodies in alcohol or benzol, in yellow needles: It is soluble in ether and in hot water, and crystallises from the latter in microscopic colourless needles. By prolonged boiling with water, it is decomposed, with continued evolution of naphthalene (Gruner, *J. pr. Chem.* cii. 222).

Trinitrophenol or ***Picric Acid.*** $C^6H^3(NO^2)^3O$.—Pure picric acid melts, according to Körner, at 122·5°; the commercial acid between 114° and 115°.

Casthelaz (*Chem. News*, xv. 140) describes a process for the testing of commercial picric acid, founded on the fact that the pure acid is soluble in ether and in benzol, whereas the impurities (oxalic acid and various salts) are insoluble in those liquids.

Picric acid digested with a concentrated aqueous solution of *iodine chloride* is converted into chloropicrin and chloranil (Stenhouse, *Chem. Soc. J.* [2] ii. 366). Under other circumstances it is converted by the same reagent into chlorodinitrophenol (p. 913).

The following *metallic picrates* have been examined by D. Müller (*Pogg. Ann.* cxxiv. 103) $[NO^2 = X]$:

Manganous salt,	$(C^6H^2X^3O)^2Mn + 5H^2O$,	light yellow rhombic crystals.
Cupric salt,	$(C^6H^2X^3O)^2Cu + 16H^2O$,	green quadratic crystals.
Cadmium salt,	$(C^6H^2X^3O)^2Cd + 7H^2O$,	light yellow rhombic crystals.
Ferrous salt,	$(C^6H^2X^3O)^2Fe + 5H^2O$,	light brown crystals permanent below 100°.
Sodio-magnesic salt,	$\left\{\begin{matrix}(C^6H^2X^3O)^2Mg\\ 3C^6H^2X^3ONa\end{matrix}\right\} + 9H^2O$,	yellow cauliflower-like crystalline groups.
Sodio-ferrous salt,	$\left\{\begin{matrix}(C^6H^2X^3O)^2Fe\\ 6C^6H^2X^3ONa\end{matrix}\right\} + 12H^2O$,	„ „ „
Sodio-cobaltous salt,	$\left\{\begin{matrix}(C^6H^2X^3O)^2Co\\ 6C^6H^2X^3ONa\end{matrix}\right\} + 12H^2O$,	„ „ „
Sodio-nickel salt,	$\left\{\begin{matrix}(C^6H^2X^3O)^2Ni\\ 6C^6H^2X^3ONa\end{matrix}\right\} + 12H^2O$,	„ „ „
Sodio-zinc salt,	$\left\{\begin{matrix}(C^6H^2X^3O)^2Zn\\ 6C^6H^2X^3ONa\end{matrix}\right\} + 12H^2O$,	„ „ „
Sodio-cadmic salt,	$\left\{\begin{matrix}(C^6H^2X^3O)^2Cd\\ 6C^6H^2X^3ONa\end{matrix}\right\} + 12H^2O$.	„ „ „
Aluminium salt,	$4C^6H^2X^3O . Al^2O^3 + 16H^2O$,	yellow needles.
Ferric salt,	$4C^{12}H^2X^3O . Al^2O^3 + 16H^2O$,	reddish-yellow needles.

1 pt. of *potassium picrate* requires for solution: of water, 273·3 pts. at 0°, and 440·8 pts. at 20°; of alcohol, 1138 pts. at 0°, and 735·5 pts. at 20° (Frisch, *J. pr. Chem.* c. 229).

Picrate of Triethylrosaniline is one of the varieties of aniline green (Alfraisse, *Dingl. pol. J.* clxxxvi. 324; *Jahresb.* 1867, p. 964).

Ethyl Picrate, $C^6H^2(NO^2)^3O . C^2H^5$, is easily obtained by digesting dry silver picrate (prepared by mixing a hot solution of picric acid with silver carbonate, boiling for a few minutes and filtering) with five times its weight of ethyl iodide at 100°, distilling off the excess of the latter, and repeatedly treating the residue with hot alcohol. The ether, when washed and repeatedly crystallised from alcohol, forms slightly yellowish needles an inch or two long, becoming darker on exposure to light. It is somewhat soluble in hot water, also in ethyl iodide, common ether, carbon bisulphide, and benzol; melts at 78·5°, solidifies at 73°, and decomposes with slight detonation at a higher temperature (H. Müller a. Stenhouse, *Chem. Soc. J.* [2] iv. 235).

Picrates of Hydrocarbons.—Picric acid, as already shown by Fritzsche (iv. 405), affords characteristic reactions for the detection of certain hydrocarbons. For this purpose it is convenient to use an alcoholic solution of the acid saturated at 20°–30°, and either: (1) add the hydrocarbon to the cold-saturated alcoholic solution; or

Hydrochloride,	$C^{20}H^{24}N^2O^2.HCl + 2H^2O$,	long asbestos-like prisms; anhydrous at 120°; sol. in 39·4 pts. water at 10°.
Dihydriodide,	$C^{20}H^{24}N^2O^2.2HI + 5H^2O$,	prisms and laminæ; anhyd. at 1[illegible].
Benzoate,	$C^{20}H^{24}N^2O^2.C^7H^6O^2$,	small prisms, sol. in 373 pts. water at 10°.
Eugenate,	$C^{20}H^{24}N^2O^2.C^{10}H^{12}O^2$,	long silky prisms, melting to an oil in boiling water; soluble in 1[illegible] pts. ether at 10°; melting, with loss of acid, at 110°.
Oxalates,	$2C^{20}H^{24}N^2O^2.C^2H^2O^4 + 6H^2O$,	long prisms; efflorescent; sol. in 1030 pts. water at 10°.
	$C^{20}H^{24}N^2O^2.C^2H^2O^4 + H^2O$,	small prisms, easily soluble in [illegible] water.
Succinate,	$C^{20}H^{24}N^2O^2.C^4H^6O^4 + 8H^2O$,	long white prisms, easily sol. in hot water or alcohol; sol. in 1030 pts. water at 10°.
Citrates,	$2C^{20}H^{24}N^2O^2.C^6H^8O^7 + 7H^2O$,	prisms, sol. in 930 pts. water at 1[illegible].
	$C^{20}H^{24}N^2O^2.C^6H^8O^7$,	prisms, slightly sol. in water.
Phosphate,	$2C^{20}H^{24}N^2O^2.PH^3O^4 + 8H^2O$,	tufts of long needles, sol. in 754 pts. water at 10°.
Arsenate,	$2C^{20}H^{24}N^2O^2.AsH^3O^4 + 8H^2O$,	long prisms, easily soluble in hot, sparingly in cold water.

Zinco-chlorides.—An alcoholic solution of quinine mixed with zinc chloride, and then with sufficient hydrochloric acid to redissolve the precipitate, deposits flattened prisms of the double salt $2(C^{20}H^{24}N^2O^2.2HCl).ZnCl^2 + 2H^2O$. A solution of this salt in dilute sulphuric acid, or a hot alcoholic solution of acid quinine hydrochloride mixed with zinc chloride, yields the salt $2(C^{20}H^{24}N^2O^2.3HCl).ZnCl^2 + 3H^2O$, which is easily soluble, and crystallises in wavellitic groups (Gräfinghoff, *Bull. Soc. Chim.* [2] iv. [illegible]).

According to R. Hauer (*Zeitschr. f. Chem.* [2] i. 481), **Herapath's** sulphate of iodoquinine (v. 25) has, when dried over sulphuric acid, the composition $4C^{20}H^{24}N^2O^2.3H^2SO^4.I^6 + 3H^2O$, and gives off its water (2·24 p. c.) at 100° in a stream of air. Quinine acetate likewise forms a crystallisable compound with iodine.

A very dilute solution of quinine mixed with about 3 mol. hydrochloric acid and 3 mol. potassium iodide, and left to itself in a loosely covered vessel, deposits crystals of the compound $4C^{20}H^{24}N^2O^2.3HCl.3HI.I^4$. Herapath's salt may be obtained in a similar manner. A warm alcoholic solution of *methyl-quinine hydriodide*, mixed with a sufficient quantity of iodine and left to cool slowly, deposits black prisms of *methyl-quinine tri-iodide*, $C^{20}H^{23}(CH^3)N^2O^2.HI^3$. An isomorphous compound of ethyl-quinine is obtained in a similar manner (Jörgensen, *Zeitschr. f. Chem.* [2] v. 674).

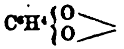
Platinosocyanides.—The neutral salt, $2(C^{20}H^{24}N^2O^2.HCy).PtCy^2 + 2H^2O$, is obtained by adding platinous cyanide to a warm solution of neutral quinine sulphate, as an amorphous precipitate, melting with decomposition at 150°–160° to a light brown liquid; not sensibly soluble in dilute hydrochloric acid. The *acid salt* $C^{20}H^{24}N^2O^2.2HCy.PtCy^2 + 2H^2O$, obtained in like manner with acid quinine sulphate, forms microscopic tabular striated crystals, which cannot be dehydrated without decomposition, and are but slightly soluble in dilute acids. Of alcohol of sp. gr. 0·[illegible] at 16°, the neutral salt dissolves in less than 5 pts. at 18°, and in all proportions at the boiling heat; the acid salt in 1270 pts. at 19°, and in 834 pts. at the boiling heat. Of water, the neutral salt dissolves in 1852 pts. at 18°, and in 56·5 pts. at 100°; the acid salt in 1351·3 pts. at 18·5°, and in 20 pts. at 100° (van der Burg, *Jahresb.* 1865, p. 440).

A compound of quinine and *phenol*, $C^{20}H^{24}N^2O^2.C^6H^6O$, is obtained by gradually adding an alcoholic solution of 8·72 pts. quinine sulphate to an alcoholic solution of 3 pts. potassium phenate, filtering after 24 hours, and evaporating at a gentle heat. It forms beautiful crystals, easily soluble in alcohol and acids, nearly insoluble in water and ether (Romei, *Zeitschr. f. Chem.* [2] v. 383).

Dihydroxyl-quinine, $C^{20}H^{26}N^2O^4 = C^{20}H^{24}N^2O^2.(HO)^2 = C^{20}H^{24}N^2O^2 + H^2O + O$ (Kerner, *Zeitschr. f. Chem.* [2] v. 593).—A compound produced by treating quinine with potassium permanganate in quantity not sufficient to produce complete oxidation. When about 1 pt. of the permanganate is used to 2 pts. of quinine, about a third part of the quinine is converted into dihydroxyl-quinine, while another portion remains unaltered, and a third portion is converted into ammonia, carbon dioxide, and greasy resinous products rich in carbon. It is also formed in the passage of quinine through the animal organism, being found in small quantity in the urine.

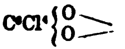
Dihydroxyl-quinine crystallised from water with addition of animal charcoal forms small, hard, colourless prisms having a vitreous lustre; from alcohol it crystallises in long, silky needles. The crystals contain $C^{20}H^{26}N^2O^4.3H^2O$. It dissolves but sparingly in water and in alcohol, more freely in presence of free alkali or of a large quantity of a strong acid; in very dilute acids, on the contrary, it is less soluble than in pure water. It is tasteless and neutral to vegetable colours, but resembles the alkaloïds in being precipitated from aqueous and acid solution by tannic acid, potassium di-iodide, potassio-mercuric iodide, and platinic chloride, and from aqueous, acid, and alcoholic solutions by the phosphometallic acids of molybdenum, tungsten, antimony, and vanadium. It exhibits a blue fluorescence in nitric acid solution, and produces with chlorine-water and ammonia a green colour similar to that obtained with quinine. Potassium permanganate attacks it but slowly in the cold and in alkaline solution; but when heated in acid solution with excess of permanganate, it is completely oxidised. Its solutions are coloured brown, like those of quinine, by prolonged exposure to the sun.

QUINONE and **HYDROQUINONE.** Graebe (*Zeitschr. f. Chem.* [2] 478) represents quinone, tetrachloroquinone (chloranil), and hydroquinone by the following formulæ:



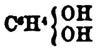
$C^6H^4\left\{\begin{matrix}O\\O\end{matrix}\right.$

Quinone



$C^6Cl^4\left\{\begin{matrix}O\\O\end{matrix}\right.$

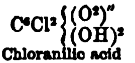
Tetrachloroquinone



$C^6H^4\left\{\begin{matrix}OH\\OH\end{matrix}\right.$

Hydroquinone

which indicate that in quinone and tetrachloroquinone the two oxygen-atoms are united together by one of their affinities, thereby constituting a bivalent group, whereas in hydroquinone this association is broken up by the entrance of the hydrogen. The same relation holds good between chloranilic and hydrochloranilic acid:



$C^6Cl^2\left\{\begin{matrix}(O^2)''\\(OH)^2\end{matrix}\right.$

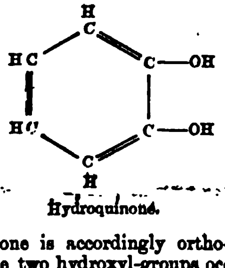
Chloranilic acid
(Dichlorodioxyquinone).

$C^6Cl^2(OH)^4$

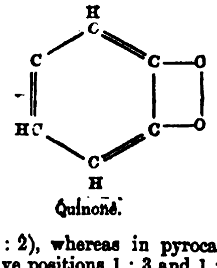
Hydrochloranilic acid
(Dichlorotetroxybenzene).

This mode of viewing the constitution of quinone explains the circumstance that when quinone is acted upon by chlorine, the ultimate product is not C^6Cl^8, but only hexchlorobenzene, C^6Cl^6, together with free chlorine.

Of the three modifications of oxyphenol, $C^6H^6O^2$, hydroquinone, pyrocatechin, and resorcin, hydroquinone is the only one which is convertible into a compound containing 2 at. hydrogen less, viz. quinone. Hence it appears most probable that in hydroquinone the two hydroxyl-groups are attached to contiguous carbon-atoms, so that the developed formulæ of quinone and hydroquinone are:



Hydroquinone.



Quinone.

Hydroquinone is accordingly ortho-oxyphenol (1 : 2), whereas in pyrocatechin and resorcin the two hydroxyl-groups occupy the relative positions 1 : 3 and 1 : 4.

In tetrachloroquinone two of the chlorine-atoms are easily replaceable by OH, NH^2, and SO^3H, giving rise to such compounds as chloranilamide or dichloramidoquinone, $C^6Cl^2(NH^2)^2(O^2)''$, chloranilamic acid or dichloramidoxyquinone, $C^6Cl^2(NH^2)(OH)(O^2)''$, &c. These replaceable chlorine-atoms appear to be the two which are nearest to the two connected oxygen-atoms: for Graebe has shown, by comparison of a large number of known examples, that a chlorine-atom joined to a carbon-atom is most easily replaceable when the same carbon-atom is also united with oxygen, or connected with another carbon-atom having oxygen attached to it.

Brominated Quinones.

Tetrabromoquinone or **Bromanil.** $C^6Br^4O^2$.—To prepare this compound, a weighed quantity of bromine is introduced, together with ⅛ pt. iodine and 5 pts. cold water, into a flask closed with a good cork through which passes a long tube, and a quantity of phenol equal to $\frac{1}{10}$ the weight of the bromine is slowly poured in th the tube. A violent reaction takes place, and the vessel becomes very hot. phenol adhering to the sides of the tube is then washed down with 5 pts. water, and the whole is heated to 100° for an hour or two. After cooling, th solid contents of the flask are collected on a filter, freed from mother-liq completely as possible by means of a Bunsen's pump (p. 617), and digested twice in the cold with carbon bisulphide, to remove tribromophenol formed same time. The tetrabromoquinone then remains in crystalline scales, very like tetrachloroquinone, which are purified by treating them once or twice with alcohol, and recrystallising from benzol (Stenhouse, *Chem. Soc. J.* [2] viii. 9).

Aniline added in excess to a solution of bromanil in hot benzol, forms bromani phenylamide, $(C^6H^5)^2(C^6Br^2O^2)H^2N^2$, in nearly black, crystalline laminæ, may be purified by washing with boiling alcohol (Stenhouse).

Bromanilic acid, $C^6Br^2\left\{\begin{matrix}(O^2)''\\(OH)^2\end{matrix}\right.$, is prepared like chloranilic acid, which it resembles. Nitric acid converts it into bromopicrin and oxalic acid. With alkaline sulphites, it yields salts of disulphodibromhydroquinonic acid, $C^6\left\{\begin{matrix}(OH)^2\\Br^2\\(SO^3H)^2\end{matrix}\right.$, and th cronic acid, $C^6\left\{\begin{matrix}OH\\(SO^3H)O.\\(SO^3H)^4\end{matrix}\right.$ With sulphurous acid, however, it does not appear to y the acid corresponding to Koch's hydrochloranilic acid.

When 3 pts. bromine are gradually added, with stirring, to 1 pt. bromanilic a suspended in 8 pts. cold water, the acid dissolves, forming a yellow liquid, which af 24–48 hours, deposits crystals of the compound $C^6Br^{11}HO$, which, when recrysta from carbon bisulphide, forms colourless, transparent prisms melting at 110·5°, ea soluble in ether, carbon bisulphide, and benzol, and dissolving in alcohol with decomposition.

Tetrabromhydroquinone or **Bromhydranil,** $C^6H^2Br^4O^2$, is formed by th action of aqueous sulphurous acid on bromanil, but considerable loss arises from th formation of secondary products. The theoretical quantity of bromhydranil ma however, be obtained by digesting bromanil with hydriodic acid and phosphorus.

Tribromhydroquinone, $C^6H^3Br^3O^2$, is formed, together with the preced compound, when sulphurous acid gas is passed through boiling water in wh bromanil is suspended; it remains in solution, and may be separated with lea carbonate, and purified in the same manner as trichlorhydroquinone (p. 987); the product is however but small. It resembles trichlorhydroquinone in its phys properties.

When the preceding solution was evaporated, and then mixed with potas chromate and sulphuric acid, a brownish-yellow precipitate was formed, which, after recrystallisation from dilute alcohol, exhibited the composition of tribromoquinone, $C^6HBr^3O^2$ (Stenhouse, *loc. cit.*).

Chlorinated Quinones and *Hydroquinones.*

(Carius, *Ann. Ch. Pharm.* cxliii. 315; *Zeitschr. f. Chem.* [2] iv. 17; *Jahresb.* 1867. p. 644. Koch, *Zeitschr. ibid.* 202; *Jahresb.* 1867, p. 646. Graebe, *Ann. Ch. Pharm.* cxlvi. 1. *Zeitschr. ibid.* 464; *Jahresb.* 1867, p. 649. Stenhouse, *Chem. Soc. J.* [2] vi. 141; viii. 6).

Dichloroquinone, $C^6H^2Cl^2O^2$, is produced by the action of chlorous anhydride on benzene. On distilling the liquid, after a considerable quantity of the gas has been passed into it, benzene passes over first, then chlorobenzene, and the residue boiling above 135° solidifies almost wholly to crystals of dichloroquinone. The first product of the action is probably dichlorohydroquinone, which, by the further action of the chlorous anhydride and the benzene, is converted into chlorobenzene and dichloroquinone:

$$1.\ C^6H^6 + Cl^2O^3 = H^2O + C^6H^4Cl^2O^2;$$
$$2.\ 2C^6H^6 + 2C^6H^4Cl^2O^2 + Cl^2O^3 = 2C^6H^5Cl + 2C^6H^2Cl^2O^2 + 3H^2O.$$

Dichloroquinone is more easily obtained, together with chlorobenzene and trichlorophenomalic acid (p. 917), by dissolving 48 grms. benzene in 300 grms. strong sulphuric acid, in loosely stoppered flasks, diluting with 150 grms. water, adding 100 grms. benzene after cooling, and then gradually adding 150 grms. potassium chlorate. At a temperature of 18° to 20°, the reaction is completed in a week. The flasks are then heated by immersion in water to 60°–70°; water is added in sufficient quantity to dissolve the potassium sulphate; and the supernatant benzene solution is separated by a pipette from the watery liquid, washed with water to remove trichlorophenomalic acid, and subjected to fractional distillation. The dichloroquinone may be extracted from the residue by hot alcohol, and crystallises therefrom in deep yellow, strongly lustrous, short prisms and tables, often joined together by their acuter summits. In very dilute solution it is quickly decomposed by potash or baryta, the liquid acquiring a deep green, or, if excess of alkali is present, a brown colour. The change appears to consist in the formation of dichlorhydroquinone, together with a very unstable chlorinated acid not yet examined:

$$2C^6H^2Cl^2O^2 + KHO = C^6H^4Cl^2O^2 + C^6HKCl^2O^3.$$

When dichloroquinone is heated with saturated baryta-water, in the proportion of $C^6H^2Cl^2O^2$ to BaH^2O^2, and the baryta precipitated by sulphuric acid, dichlorhydroquinone may be extracted from the filtrate by ether, together with a humus-like substance, whilst the aqueous solution retains a small quantity of an easily soluble amorphous acid (Carius).

Trichloroquinone, $C^6HCl^3O^2$, is produced, together with tetrachloroquinone, by gradually adding a mixture of 1 pt. crystallised phenol and 4 pts. potassium chlorate to gently warmed hydrochloric acid diluted with an equal bulk of water, then adding more potassium chlorate by small portions till the separated crystals have turned yellow, washing these crystals with cold water, and finally digesting them with cold alcohol, as long as this liquid acquires a yellow colour. This product (as also that obtained in like manner from phenylsulphuric acid or from salicin, v. 29) is a mixture of tri- and tetra-chloroquinone in about equal quantities. These two compounds cannot be separated by crystallisation from alcohol, but their separation is easily effected by first converting them into the corresponding hydroquinones. For this purpose the crystalline mass is suspended in water and saturated with sulphurous acid, then left to itself for 24 hours, heated to boiling when it has become colourless, and the residue is repeatedly boiled with water, which takes up the greater part of the trichlorhydroquinone, leaving the tetrachlorhydroquinone mixed with a small quantity of trichlorhydroquinone. The trichlorhydroquinone separates from the solution in large crystals. On slowly dropping nitric acid into the hot filtrate, nitrogen dioxide is given off, and trichloroquinone immediately separates in yellow crystals. The same treatment may be advantageously applied to the mother-liquor of the crystallised trichlorhydroquinone (ferric chloride may also be used as the oxidising agent instead of nitric acid). The tetrachlorhydroquinone is purified by recrystallisation from alcohol, acetic acid, or benzol, but still retains a small quantity of trichlorhydroquinone, which adheres to it obstinately. By treatment with nitric acid, or with potassium chlorate and hydrochloric acid, it is converted into tetrachloroquinone (Graebe). On the preparation and purification of these products, see also Stenhouse (*Chem. Soc. J.* [2] vi. 203).

Trichloroquinone prepared as above agrees in all its properties with that which Städeler obtained (v. 28) from quinic acid (melting point 164° to 166°; Städeler found 160°). Dilute potash colours it green and then dissolves it with red-brown colour, forming chloranilic acid, the potassium salt of which separates after a while in needles:

$$C^6HCl^3O^2 + 2KHO = C^6Cl^2(KO)^2O^2 + HCl + H^2.$$

Phosphorus pentachloride does not act on trichloroquinone under ordinary pressure; but on heating the mixture to 180°–200° in a sealed tube, with addition of phosphorus oxychloride, the trichloroquinone is converted into perchlorobenzene, according to the equation:

$$C^6HCl^3O^2 + 2PCl^5 = C^6Cl^6 + 2POCl^3 + HCl.$$

With *acetyl chloride*, trichloroquinone forms diacetyl-tetrachlorhydroquinone:

$$C^6HCl^3O^2 + 2C^2H^3OCl = HCl + C^6Cl^4(C^2H^3O^2)^2.$$

Trichlorhydroquinone, $C^6H^3Cl^3O^2$, prepared as above, crystallises in large shining prisms, which become turbid in contact with the air. It melts at 134° (at 130° according to Städeler, iii. 216), dissolves sparingly in cold water, more easily in hot water (in which it first melts), very easily in alcohol and in ether. The aqueous solution gradually turns brown in contact with the air, from formation of hexchloroquinhydrone. Lead acetate throws down from it the lead salt, $C^6HCl^3O^2Pb$, which dissolves easily in acetic acid, and turns brown when exposed to the air in the moist

$C^6H^3(NH^2)^3.3HI$, by the action of iodine and phosphorus on picric acid, and regards the salt which Heintzel obtained by the same process, not as the hydriodide of triamidophenol, but as the trihydriodide of picramine contaminated with phosphoric acid.

Triamidophenol. $C^6H^2(NH^2)^3OH$.—A mixture of 1 pt. picric acid, 4 pts. tin, and 15 pts. crude hydrochloric acid, when gently warmed, begins to boil in a few minutes, and the filtered liquid deposits on cooling quadratic laminæ, which after drying over lime in a vacuum, have, according to Heintzel, the composition of *triamidophenol stannochloride*, $C^6H^2(NH^2)^3OH.3HCl.SnCl^2$ [according to Beilstein, that of picramine stannochloride, $C^6H^3(NH^2)^3.3HCl.SnCl^2$]. This salt dissolves in water, alcohol, and ether, and after recrystallisation from water contains 1½ mol. water (5·8 p. c.). It is partially decomposed by repeated crystallisation from a slightly acid aqueous solution, but from a solution containing a large excess of hydrochloric acid it separates without decomposition in fan-shaped groups of long needles. The alcoholic or ethereal solution of the salt acquires a deep blue colour; so likewise does the aqueous solution when much diluted; ferric chloride produces the same colour. The *hydrochloride*, $C^6H^2(NH^2)^3OH.3HCl$, obtained by removing the tin from the preceding salt by hydrogen sulphide, is easily soluble in water, less soluble in alcohol and ether, and separates by slow evaporation in a vacuum, in nodular groups of yellow needles; the concentrated solution imparts a permanent green-black colour to the skin, also to wool and silk. The *sulphate*, $2C^6H^2(NH^2)^3OH.3SO^4H^2$, is deposited on mixing the concentrated solution of the hydrochloride with dilute sulphuric acid, in white curdy flocks, which when moist gradually change to dark-coloured rhombohedral crystals. The *hydroferrocyanide*, $2C^6H^2(NH^2)^3OH.Fe^2H^4Cy^6$, is a white crystalline precipitate, slightly soluble in water and in alcohol; potassium ferrocyanide also forms a white precipitate.

Amido-diimidophenol Hydrochloride, $C^6H^2(NH^2)(NH)^2OH.HCl$ * (?), is gradually deposited from a concentrated solution of triamidophenol hydrochloride, in brown crystals having a blue lustre by reflected light, insoluble in ether, slightly soluble in alcohol, easily and with splendid blue colour in water; decomposed by hot water. The blue solution heated with dilute hydrochloric or sulphuric acid becomes red, and deposits white needles, having nearly the composition of the *hydrochloride of amid-imid-hydroxyphenol*, $C^6H^2(NH^2)(NH)(OH)^2.HCl$ * (?) (Heintzel).

PHENOLIC ETHERS. *Ethyl-phenol* or *Phenetol.* $C^8H^{10}O = C^6H^5.(C^2H^5)O$ (Fittig a. Kiesow, *Zeitschr. f. Chem.* [2] v. 333. Beilstein a. Kuhlberg. *ibid.* 461; *Chem. Centr.* 1870, 45).—This compound, originally obtained by the dry distillation of barium ethyl-salicylate (iv. 391), may also be prepared by heating the potassium salt of ethyl-benzene-sulphuric acid with 3 pts. of potassium hydrate to 270°–280° for some hours, acidulating with sulphuric acid, and distilling. The ethyl-phenol, which passes over with the first portions of aqueous vapour, is separated from the water, left some time in contact with calcium chloride, and subjected to fractional distillation, the greater part passing over between 208° and 210°. This portion solidifies on cooling in large transparent prismatic crystals, very much like phenol, which may be freed from an adhering viscid oil by pressure between bibulous paper in the exsiccator. The crystalline compound is ethyl-phenol. It melts at 47°–48° and boils at 209°–210° (Fittig a. Kiesow); melts at 46° and boils at 214°–215° (Beilstein a. Kuhlberg), but volatilises even at ordinary temperatures. In contact with water it instantly liquefies, whence it seems to follow that liquid ethyl-phenol (iv. 391) is rather a hydrate than an isomeric modification (Fittig a. Kiesow). On the other hand, the liquid ethyl-phenol expressed from the crystals as above mentioned does not solidify even in a freezing mixture; it boils at 212° (Beilstein a. Kuhlberg).

Ethyl-phenol treated with sodium and carbon dioxide is converted into ethyl-(para- or meta-) oxybenzoic acid: $C^6H^5(C^2H^5)O + CO^2 = C^7H^5(C^2H^5)O^3$ (Beilstein a. Kuhlberg). See PARAOXYBENZOIC ACID (p. 899).

Methyl-phenol. $C^6H^5(CH^3)O$.—See ANISOL (i. 365).

Chloromethyl-phenol, $C^6H^4Cl(CH^3)O$, is produced by the action of phosphorus pentachloride on anisol. It is a colourless liquid having a rather agreeable odour, a sp. gr. of 1·182 at 9°, and boiling at about 200°. Insoluble in water and in alkalis, soluble in alcohol and in ether; dissolved by strong nitric acid with rise of temperature, but without evolution of gas (L. Henry, *Zeitschr. f. Chem.* [2] vi. 247).

Bromethyl-phenol, $C^6H^4Br(CH^3)O$, obtained in like manner, boils at 220°, and has a sp. gr. of 1·494 at 9° (Henry).

Chlorethyl-phenol, $C^6H^4Cl(C^2H^5)O$, resembles the methyl-compound in external character, boils at 210°, and has a sp. gr. of 1·106 at 9° (Henry).

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* These formulæ are inadmissible, inasmuch as the imidogen, which is essentially a bivalent radicle, enters into them as univalent.

chloranil moistened with alcohol, to very dilute potash-ley (containing 1 p. c. potassium hydrate) heated to about 50°, and agitating as long as anything is taken up; the liquid is then filtered warm, evaporated to one half, and strong potash-ley is added to it by drops till a quickly cooled sample solidifies in crystals. The salt then crystallises after a few hours in beautiful purple-red prisms, and the remainder may be separated from the mother-liquor by evaporation and passage of carbon dioxide (Graebe); see also Stenhouse (*Chem. Soc. J.* [2] viii. 6).

Chloranilic acid heated with sp. gr. 1·45 yields oxalic acid and a distillate of chloropicrin. By chlorine, or more quickly by iodine-chloride in presence of water, it is converted into oxalic acid and a heavy oil. The acid suspended in water is converted by bromine into a white crystalline body, having the composition $C^6Br^3Cl^3HO$. This compound dissolves easily in carbon bisulphide, and crystallises therefrom by spontaneous evaporation in very large prisms. In alcohol it dissolves with decomposition, the solution when evaporated, even at ordinary temperatures, giving off alcohol, and leaving an oil. It dissolves easily in benzol and in ether, melts at 79·5°, and distils without decomposition. It does not appear to be attacked by boiling sulphuric acid (Stenhouse).

Ethyl Chloranilate, $C^6Cl^2(C^2H^5)^2O^4$, obtained by decomposing silver chloranilate with ethyl iodide, crystallises in smooth bright red prisms, melting at 107°, soluble in benzol, light American oil, carbon bisulphide, and ether, moderately soluble in alcohol, somewhat soluble in boiling water (Stenhouse).

Hydrochloranilic Acid or **Dichlorotetrahydroxybenzene.** $C^6Cl^2H^4O^4 = C^6Cl^2(HO)^4$ (Koch; Graebe, *loc. cit.*).—This compound is produced by the action of reducing agents on chloranilic acid, as when sodium-amalgam is gradually added to a solution of the latter acid, or its potassium salt, kept slightly acid by addition of hydrochloric acid, till the liquid is decolorised and hydrogen begins to escape. Hydrochloranilic acid then crystallises out, and may be purified by washing with water, pressing between paper, and drying over sulphuric acid in a vacuum. The reduction may also be effected by tin and hydrochloric acid, or by heating chloranilic acid to 100° for several hours in a sealed tube with saturated aqueous sulphurous acid. When the liquid has become colourless and cold, the tube is opened, the excess of sulphurous acid removed by a current of carbonic acid gas, and the solution is left to crystallise out of contact with the air (Koch). Graebe regards this last mode of preparation as the best.

Hydrochloranilic acid forms colourless needles easily soluble in water, alcohol, and ether, inodorous, having a burning taste, and slight acid reaction. It is permanent in the dry state, but when moist is easily oxidised to chloranilic acid by the action of air, chlorine, or bromine. With alkalis it forms solutions which are colourless at first, but turn red on exposure to the air, and gradually deposit a salt of chloranilic acid. The solution of the acid quickly reduces silver nitrate, and forms with barium chloride and cupric sulphate, on addition of ammonia, green precipitates, which quickly turn brown on exposure to the air.

Hydrochloranilic Chloride. $C^6Cl^2\begin{cases}Cl^2\\(HO)^2\end{cases}$.—When 1 mol. hydrochloranilic acid is heated with 2 mol. phosphorus pentachloride, hydrochloric acid and phosphorus oxychloride are given off, and the partially carbonised residue yields with water a yellow solution which deposits hydrochloranilic chloride in colourless needles. This compound, isomeric with tetrachlorhydroquinone, is formed as shown by the equation:

$$C^6H^4Cl^2O^4 + 2PCl^5 = C^6H^2Cl^2O^2.Cl^2 + 2POCl^3 + 2HCl.$$

It is more permanent than the acid, dissolves with yellow colour in water and alcohol, and may be recrystallised without decomposition. It is distinguished from tetrachlorhydroquinone by its easy solubility in water. Its solutions slowly decompose, with formation of chloranilic acid, and are coloured dark green by ferric chloride. Heated to 100° in a stream of dry chlorine, it is converted, with evolution of hydrochloric acid and a volatile strong-smelling oil, into a red unctuous mass, which hardens in a vacuum over quick lime, but quickly deliquesces in the air, and dissolves with red colour in water. Silver nitrate throws down from this solution a brown crystalline precipitate, $C^6Cl^4Ag^2O^4$, which is permanent in dry air, and detonates when quickly heated. The product formed by the action of chlorine appears therefore to be *dichlorhydrochloranilic acid*, $C^6Cl^4H^2O^4$; by water and by bases at the boiling heat it is quickly converted into chloranilic acid (Koch).

Tetraceto-hydrochloranilic acid, or *Dichloro-tetracetoxybenzene*, $C^6Cl^2(C^2H^3O^2)^4$, is formed by heating hydrochloranilic acid with acetyl chloride to 100° in a sealed tube. On expelling the excess of acetyl chloride on the water-bath, washing the resulting crystals with water, and recrystallising from alcohol, the dichlorotetracetoxybenzene separates in colourless needles, insoluble in water, slightly soluble in cold alcohol and ether, more easily in boiling alcohol. It sublimes without decomposition in long needles, melts at 235°, and is very stable, not being attacked by weak oxidising agents, or by cold potash-ley. Boiling potash slowly converts it into chloranilate and acetate of potassium. Koch's hydrochloranilic chloride is regarded by Graebe as a tetrachlorinated substitution-product of pyrocatechin or resorcin.

Tetrachlorotetroxyquinhydrone, $C^{12}Cl^4H^4O^8$, is formed by the incomplete reduction of chloranilic acid by sulphurous acid, or when hydrochloranilic acid is oxidised by exposure to the air. It crystallises in slender black needles; is converted by oxidation into chloranilic acid, and by further treatment with sulphurous acid into hydrochloranilic acid (Graebe).

Sulpho-acids derived from the Chlorinated Quinones and Hydroquinones.

The salt described by Hesse (v. 22) as potassium disulphodichlorosalicylate is, according to Graebe's analysis, the potassium salt of *dichlorhydroquinone-disulphuric acid*, $C^6Cl^2S^2H^2K^2O^8$. It is produced by adding tetrachloroquinone to a warm dilute solution of acid potassium sulphite:

$$C^6Cl^4O^2 + 3H(SO^3K) = C^6\left\{\begin{matrix}(OH)^2\\ Cl^2\\ (SO^3K)^2\end{matrix}\right. + 2HCl + KHSO^4.$$

Thiochronic Acid. $C^6H^6S^5O^{17}$.—The potassium salt of this acid, which Hesse obtained by the action of acid potassium sulphite on tetrachloroquinone, is conveniently prepared, according to Graebe, by saturating a slightly warmed dilute solution of neutral potassium sulphite with tetrachloroquinone, separating the yellow crystals which are deposited on cooling, from the lighter white crystals of the preceding salt formed at the same time, finally recrystallising it from water, and boiling it with alcohol to remove the last portions of the white salt. The air-dried thiochronate has the composition $C^6HS^5K^5O^{17} + 4H^2O$, and gives off 3 mol. water, at 130°. In its formation, the chlorine of the tetrachloroquinone is replaced by the group SO^3K, and the resulting compound, $C^6\left\{\begin{matrix}O^2\\ (SO^3K)^4\end{matrix}\right.$, unites with 1 mol. acid potassium sulphite, forming the thiochronate, $C^6\left\{\begin{matrix}OH\\ O(SO^3K)\\ (SO^3K)^4\end{matrix}\right.$. Heated with water in a sealed tube, it is resolved into *hydroquinone-disulphate* and acid sulphate of potassium, according to the equation:

$$C^6\left\{\begin{matrix}OH\\ O(SO^3K)\\ (SO^3K)^4\end{matrix}\right. + 3H^2O = C^6\left\{\begin{matrix}(OH)^2\\ H^2\\ (SO^3K)^2\end{matrix}\right. + 3KHSO^4.$$

The crystallised salt undergoes the same decomposition when quickly heated to 100°, and in dilute hydrochloric solution even at 100°. The hydroquinone-disulphate is also produced from the thiochronate, together with acid sulphite, by the action of reducing agents, as by boiling the solution with zinc-dust, or treating it with sodium-amalgam and hydrochloric acid. The attempt to prepare other salts of thiochronic acid was not successful.

Euthiochronic acid, produced by the action of alkalis on thiochronic acid, and regarded by Hesse (*Ann. Ch. Pharm.* cxiv. 292) as $C^6H^4S^2O^8$, by Greiff (*Jahresb.* 1863, p. 392) as $C^6H^6S^2O^{10}$, is, according to Graebe, *dioxyquinone-disulphuric acid*, $C^6H^4S^2O^{10} = C^6\left\{\begin{matrix}O^2\\ (OH)^2\\ (SO^3H)^2\end{matrix}\right.$. The formation of the potassium salt by the action of potash on the thiochronate, or on the dichlorhydroquinone-disulphate (in the latter case with aid of atmospheric oxygen), is represented by the following equations:

$$\underset{\text{Thiochronate.}}{\left\{\begin{matrix}OH\\ O(SO^3K)\\ (SO^3K)^4\end{matrix}\right.} + 2KOH = \underset{\text{Euthiochronate.}}{C^6\left\{\begin{matrix}(O^2)''\\ (OK)^2\\ (SO^3K)^2\end{matrix}\right.} + \underset{\text{Acid sulphite.}}{3KHSO^3}$$

$$\underset{\text{Dichlorhydroquinone-disulphate.}}{C^6\left\{\begin{matrix}(OH)^2\\ Cl^2\\ (SO^3K)^2\end{matrix}\right.} + 2KOH + O = \underset{\text{Euthiochronate.}}{C^6\left\{\begin{matrix}(O^2)''\\ (OK)^2\\ (SO^3K)^2\end{matrix}\right.} + 2HCl + H^2O.$$

Free euthiochronic acid is obtained by exactly decomposing the barium salt with sulphuric acid, and evaporating the solution, finally over strong sulphuric acid, and crystallises in yellow needles easily soluble in alcohol and ether. The following salts have been examined:

Potassium salt,	$C^6S^2O^{10}K^4 + 2H^2O$.
Sodium salt,	$C^6S^2O^{10}Na^4 + H^2O$.
Barium salt,	$C^6S^2O^{10}Ba^2 + 4H^2O$.
Silver salt,	$C^6S^2O^{10}Ag^4$.

Hydro-euthiochronic or *Tetroxybenzene-disulphuric acid*, $C^6H^6S^2O^{10} = C^6\left\{\begin{matrix}(OH)^4\\(SO^3H)^2\end{matrix}\right.$, is produced by the action of reducing agents on euthiochronic acid. The potassium salt, $C^6H^4S^2O^{10}K^2 + 2H^2O$, is obtained, by boiling the euthiochronate with tin and hydrochloric acid, till the solution is decolorised, and evaporating the filtrate, in colourless prisms, which in the moist state quickly turn red by oxidation. It is slightly soluble in cold, more easily in hot water, forming a solution which oxidises in the air in presence of free alkali, reduces silver nitrate in the cold and mercurous nitrate at the boiling heat, forming a salt which crystallises in red needles; ferric chloride colours the solution dark brown-red. The sodium salt, $C^6H^4S^2O^{10}Na^2 + 2H^2O$, is prepared in like manner, and exhibits similar characters.

Hydroquinone-disulphuric Acid. $C^6(OH)^2H^2(SO^3H)^2$.—This acid, produced, as above mentioned, from thiochronic acid by heating with water or hydrochloric acid, is different from that which Hesse obtained by treating quinic salt with sulphuric acid (iii. 217). Graebe distinguishes this latter as α, and the acid produced from thiochronic acid as β hydroquinone-disulphuric acid. The free β acid is obtained by precipitating the potassium salt with lead acetate, decomposing the precipitate with hydrogen sulphide, and evaporating the filtrate to a syrup over sulphuric acid. It crystallises in deliquescent tables, easily soluble in alcohol, insoluble in ether. Its strongly acid solution is coloured blue by ferric chloride. The *potassium salt*, $C^6H^4S^2O^8K^2 + 4H^2O$, separates from the hot aqueous solution in large prisms, with oblique end-faces; gives off its crystallisation-water over sulphuric acid; dissolves very easily in hot, very sparingly in cold water, and is insoluble in alcohol. The solution has a neutral reaction, is coloured deep blue by ferric chloride; is not precipitated by barium or calcium chloride, and with aid of heat reduces mercuric to mercurous chloride, silver nitrate and mercurous nitrate to metal.

Trichlorhydroquinone-sulphuric Acid. $C^6\left\{\begin{matrix}(OH)^2\\Cl^3\\SO^3H\end{matrix}\right.$.—The potassium salt of this acid, $C^6(OH)^2Cl^3SO^3K + H^2O$, is formed, together with euthiochronate, by dissolving trichloroquinone in neutral potassium sulphite, and separates in colourless microscopic crystals. It reacts like the potassium salt of the preceding acid, but is soluble in alcohol. The solution mixed with potash turns red in contact with the air, and gradually deposits the potassium-salt of monochloro-dioxyquinone-sulphuric acid. The free trichlorinated acid, $C^6H^3Cl^3SO^5$, prepared like the preceding acid from the lead salt, crystallises in deliquescent needles easily soluble in alcohol and ether.

Potassium Monochlorodioxyquinone-sulphate, $C^6ClSO^7K^3 + 2H^2O$, crystallises from a solution of potassium trichlorhydroquinone-sulphate mixed with potash and exposed to the air, in red needles, while yellow-brown salts formed at the same time, but not yet examined, remain in the mother-liquor. It is easily soluble in water, both hot and cold, less soluble in alkaline liquids, insoluble in alcohol. Calcium chloride added to the aqueous solution throws down a red-violet precipitate. Hydrochloric acid added to the concentrated solution throws down the acid salt $C^6ClH^2SO^7K$ as a crystalline precipitate, which dissolves with blood-red colour in water, and crystallises from the hot-saturated solution in yellow laminæ. By tin and hydrochloric acid the neutral salt is reduced to a colourless compound not yet examined (Graebe).

R

RAHTITE. A sulphide of copper, iron, and zinc, ($\frac{2}{10}$ Cu, $\frac{1}{10}$ Fe, $\frac{7}{10}$ Zn)S, occurring together with copper pyrites and copper glance, in the copper mines of Ducktown in Tennessee. It is massive, traversed in all directions by shining prismatic cavities, has a lead-grey colour and metallic lustre, hardness = 3·5, sp. gr. = 4·128 (Tyler a. Shepard, *Sill. Am. J.* [2] xli. 209;—Credner, *Jahresb.* 1867, p. 976).

RAIMONDITE. A hydrated ferric sulphate, $2Fe^2O^3.3SO^3 + 7H^2O$, found in a tin mine in Bolivia, in extremely thin tabular hexagonal prisms having an ochre-yellow to honey-yellow colour, nacreous lustre, hardness = 4, and sp. gr. 3·190 to 3·222 (Breithaupt, *Jahresb.* 1866, p. 952).

RATANHIA-RED. This substance, first obtained by Wittstein as a product of the decomposition of ratanhia-tannic acid, may be prepared, according to Grabowski (*Ann. Ch. Pharm.* cxliii. 274), by precipitating the hot aqueous infusion of rhatany extract with lead acetate, decomposing the precipitate with hydrogen sulphide, and boiling the filtrate with dilute sulphuric acid. The red-brown powder thereby separated, when purified by solution in ammonia and precipitation with hydrochloric acid, and dried at 130°, has the composition $C^{26}H^{22}O^{11}$, which is also that of the red substance obtained by Rochleder from the tannin of the horse-chestnut. By fusion with potash, it is resolved, like the latter, into pyrocatechuic acid and phloroglucin, which two bodies are also produced by fusing rhatany extract with potash. The liquid separated from the ratanhia-red contains a difficultly crystallisable sugar.

RESINS (Hlasiwetz a. Barth, *Ann. Ch. Pharm.* cxxxiv. 265; cxxxviii. 61; cxxxix. 83; *Jahresb.* 1865, p. 573; 1866, pp. 626, 631).—The resins of very many plants yield similar products of decomposition by oxidation with potash. A considerable portion of the resin is resolved, as by dry decomposition, into volatile products, aromatic vapours, hydrocarbons, &c., while another portion, of variable amount, separates again in the resinous form; or humus-like products are formed, and in all cases, acetic acid and its nearest homologues. The principal products are: (1) *Protocatechuic acid*, $C^7H^6O^4$, from guaiacum, benzoïn, dragon's blood, asafœtida, myrrh, acaroïd resin, opoponax.—(2) *Paraoxybenzoic acid*, $C^7H^6O^3$, from benzoïn, dragon's blood, aloes, acaroïd resin.—(3) *Phloroglucin*, $C^6H^6O^3$, from dragon's blood and gamboge.—(4) *Resorcin*, from galbanum, asafœtida, gum ammoniacum, sagapenum, acaroïd resin, and probably from all resins which yield umbelliferone. *Pyrocatechin* (as also perhaps a small quantity of a body which reddens ferric chloride) probably occurs only as a secondary product resulting from the decomposition of protocatechuic acid. Orcin is formed only from aloes; isuvitic acid and pyrotartaric acid only from gamboge. (See the several Resins.)

Resins are formed artificially by the action of phosphoric anhydride on aldehydes and allied bodies. The resin formed in this manner from bitter almond oil has been already described (p. 327). *Eugene-resin*, formed in like manner from eugenic acid, is an inodorous mass having an aromatically bitter taste and exhibiting violet-blue dichroïsm in alcoholic solution. In composition it is intermediate between eugenic acid, $C^{10}H^{12}O^2$, and the next more highly oxygenised compound, $C^{10}H^{12}O^3$; by dry distillation it yields an oil which contains creosote, and colours ferric chloride green; with nitric acid it yields scarcely anything besides oxalic acid; with melting potash, considerable quantities of protocatechuic acid, together with a small quantity of acetic acid; its alcoholic solution is precipitated by neutral lead acetate. *Oil of cassia* becomes thickened in contact with phosphoric anhydride. The oils of rue, angelica, and cumin are partially converted into dark brown resins, which when fused with potash, yield only traces of a crystalline substance producing a violet colour with ferric chloride. *Oil of guaiacum* is converted into a thick (phosphoretted) oil, yielding with melting potash a large quantity of protocatechuic acid. *Anise-camphor*, $C^{10}H^{12}O$, gently heated with iodic acid and iodine in alkaline solution, is converted into a brown brittle resin, the portion of which insoluble in alcohol and soluble in ether has nearly the composition of anise-camphor. By fusion with potash it yields a small quantity of a crystalline substance having the properties of anisic acid.

On the formation of resins in the interior of vegetable cells, see Wiesner (*Wien. Akad. Ber.* lii. [2] 118; *Jahresb.* 1865, p. 627).

RESORCIN. $C^6H^6O^2 = C^6H^4(OH)^2$.—This substance, the para-modification (1 : 4) of oxyphenol, was originally obtained by the action of melting potash on galbanum (iv. 215), and is likewise produced by the same reaction: from para-iodophenol: $C^6H^5IO + KOH = KI + C^6H^6O^2$ (Körner, *Bull. Soc. Chim.* [2] vii. 261);—from paraphenolsulphuric acid: $C^6H^4(OH)(SO^3K) + KHO = K^2SO^3 + C^6H^4(OH)^2$ (Glutz, *ibid.* viii. 361);—from potassium monochlorobenzene-sulphate by fusion with about twice its weight of potassium hydrate (Oppenheim a. Vogt, *Jahresb.* 1868, p. 465);—from umbelliferone: $C^9H^6O^3 + O^5 = C^6H^6O^2 + 3CO^2$ (Hlasiwetz a. Grabowski, *Ann. Ch. Pharm.* cxxxix. 99);—and from asafœtida, gum ammoniacum, sagapenum, acaroïd resin, and probably from all resins which yield umbelliferone by dry distillation (Hlasiwetz a. Barth, p. 992).

Resorcin crystallises in prisms, which according to Reuss (*Jahresb.* 1866, p. 633) are triclinic, exhibiting the combination $\infty\bar{P}\infty \,.\, \infty\breve{P}\infty \,.\, oP \,.\, \infty P' \,.\, \infty\bar{P}2 \,.\, \infty'\breve{P}2 \,.\, {}_{,}P$. According to Rammelsberg's measurements, on the other hand (made on crystals prepared by Oppenheim a. Vogt), they are orthorhombic prisms (p), with bevelling faces (q) resting on the acute lateral edges. Angle $p : p = 118°$ to $119°$; $q : q = 83°$ to $84°$; $p : q = 112°$ to $113°$. The edge $\frac{p}{p}$ is apparently perpendicular to $\frac{q}{q}$.

On the power possessed by resorcin of masking the presence of iodine in solution, see Iodine (p. 738).

Resorcin in contact with the vapours of strong *nitric acid* is gradually converted into a dark red-brown resinous mass, soluble in water, alcohol, and ether, and coloured violet-brown in thin layers by ammonia (Malin).

Resorcin Sulphate, $C^6H^6O^2.4H^2SO^4$, crystallises very easily from a solution of 4 pts. warm concentrated sulphuric acid. The very deliquescent strongly acid compound is coloured blood-red by ferric chloride even in very dilute solution, and is easily decomposed by bases. *Quinine-resorcin sulphate*, $C^{20}H^{24}N^2O^2.C^6H^6O^2.SO^3 + 1\frac{1}{2}H^2O$, is formed by mixing 2 pts. resorcin with a slightly acidulated solution of 5 pts. quinine sulphate, and crystallises in needles (Malin).

Resorcin-ammonia, $C^6H^6O^2.NH^3$, is formed by passing dry ammonia gas into a solution of resorcin in anhydrous ether, and separates as an oil, which afterwards crystallises. The colourless crystals, when exposed to the air, deliquesce and turn green, and afterwards blue, in consequence of the formation of a product resembling orceïn, and precipitable from the alkaline solution by acids in red-brown flocks (Malin).

Acetyl-resorcin, $C^6H^4(C^2H^3O)^2O^2$, formed by the action of acetyl chloride on resorcin, is an oily liquid, colourless and inodorous after distillation, insoluble in water, and having a burning bitter taste, with sweetish after-taste. *Benzoyl-resorcin*, $C^6H^4(C^7H^5O)^2O^2$, remains, on heating resorcin to 100° with benzoyl chloride, as a red viscid mass, crystallising from hot water in white talc-like scales. The mother-liquor yields laminar crystals of a more soluble compound, probably $C^6H^5(C^7H^5O)O^2$. Both compounds are insoluble in water. With *succinyl chloride*, resorcin forms (with evolution of hydrochloric acid), a red-brown uncrystallisable oil, from whose alcoholic solution water throws down a resin, which in alkaline solution exhibits a deep green dichroïsm. When resorcin is heated with *phosphorus pentachloride*, white uncondensable vapours are evolved, and a semi-carbonised mass remains behind (Malin, *Ann. Ch. Pharm.* cxxxviii. 76).

RETENE. $C^{18}H^{18}$ (v. 97).—This hydrocarbon is produced, together with other polymerides of acetylene, when the vapour of the latter is passed through a red-hot glass tube. The liquid portion of the product subjected to fractional distillation yields several of these polymeric acetylenes, retene passing over at about 360°, and condensing in shining needles (Berthelot, *Jahresb.* 1866, p. 516). It boils at 390° (Berthelot, *ibid.* 1867, p. 39).

Wahlforss (*Zeitschr. f. Chem.* [2] v. 73) has examined retene prepared from a granular buttery mass obtained in the latter part of the distillation of Finland wood-tar. This mass was strongly pressed during a winter temperature; then fused with 10 p. c. benzol, and again pressed; afterwards divided into four fractions by fusion, pulverisation, and partial solution in alcohol; and each of these portions was repeatedly crystallised till its melting point became constant. All the samples finally exhibited a melting point of 98°–99°, the same as that assigned to retene by Fehling; by Fritzsche and Berthelot, retene is said to melt at 95°. The retene obtained as above yielded a picrate, and a barium salt of disulphoretic acid, agreeing exactly with those described by Fritzsche (v. 97).

Retene exhibits a very characteristic reaction with *chromic acid*. In contact with a mixture of 5 pts. potassium dichromate, 8 pts. sulphuric acid, and 2½ vol. water, it is strongly attacked, carbon dioxide being evolved, and the reaction going on without external heating. The solution if finally heated turns green; the retene is converted into a red powder; the filtrate when distilled yields acetic acid; and on exhausting the residual solution of chrome-alum with ether, then expelling the ether, and subliming the residue, phthalic anhydride is obtained, melting at 128°.

Dioxyretistene, $C^{16}H^{14}O^2$, the brick-red powder above mentioned, which is the chief product of the reaction, crystallises from alcohol in long, flat, orange-coloured needles, melting at 194°–195° and sublimable to a small extent. It is more soluble in ether and in benzol than in alcohol, insoluble in soda-ley; does not give off hydrochloric acid when treated with benzoyl chloride; is but slightly attacked by chromic acid; dissolves in oil of vitriol with deep green colour; its alcoholic solution is coloured by potash first a deeper red, afterwards green. With *bromine* it forms the compound $C^{16}H^{13}BrO^2$, very much like dioxyretistene itself, but somewhat lighter in colour.

Dioxyretistene heated with zinc-dust yields an oily distillate which soon solidifies and crystallises in white shining laminæ having the composition $C^{16}H^{14}$. This hydrocarbon, called retistene, forms with picric acid a compound which crystallises in long yellow-red needles melting at 94°.

REWDANSKITE. A nickel ore occurring near the Rewdansk works in the Ural. It forms indistinctly laminated lumps, which easily crumble to an earthy powder. Sp. gr. 2·77. The analysis, corresponding to the formula $3RO.2SiO^2 + 2H^2O$, yielded:

SiO^2	Al^2O^3	FeO	NiO	MgO	H^2O	Sand	
32·10	3·25	12·15	18·33	11·50	9·50	13·00	= 99·83

together with traces of manganous oxide and bismuth oxide (Hermann, *J. pr. Chem.* c. 100).

RHAMNUS. According to Kubly (*Jahresb.* 1866, p. 707), the bark of *Rhamnus Frangula* contains, besides the purgative principle, an amorphous glucoside, $C^{34}H$… called *avornin*, resolvable by acids into sugar, crystallisable *avornic acid*, $C^{32}H^{10}O^{8}$, and an amorphous resin. According to Buchner (*ibid.* 1865, p. 588), the volatile yellow substance, *rhamnoxanthin*, which he found in the bark of *Rh. Frangula* (v. 1001), is partly converted, by very slow sublimation, into a red body resembling alizarin, but more soluble in alcohol.

Colouring Matters of Rh. infectoria and Rh. tinctoria (yellow berries).—These bodies have been examined by several chemists, but with somewhat discordant results. According to Lefort (*Compt. rend.* lxiii. 840; *Jahresb.* 1866, p. 650), the berries contain, besides rhamnin, which is insoluble in water, another colouring matter, rhamnegin, having the same composition, but soluble in water. The berries of *Rh. cathartica* contain only rhamnegin. This substance, obtained by spontaneous evaporation of a concentrated alcoholic extract of yellow berries (*graines de Perse ou d'Avignon*), and purified by treatment with alcohol and ether, forms yellowish-white, cauliflower-like masses, composed of small prismatic needles easily soluble in water and in hot alcohol. By solution in cold concentrated or dilute sulphuric acid, it is converted into rhamnin without formation of sugar. The same transformation is induced by nitric acid, hydrochloric acid, and several neutral salts. It dissolves with bright yellow colour in alkalis and alkaline earths, and forms insoluble compounds with the oxides of the heavy metals. The composition of rhamnegin and of its lead and copper compounds is represented by the following formulæ:

$$C^{12}H^{12}O^5.2H^2O; \qquad C^{12}H^{12}O^5.PbO; \qquad C^{12}H^{12}O^5.CuO.$$

Rhamnin in its lead and copper compounds has the same composition. It is insoluble in water, but soluble in boiling alcohol, and reacts in other respects like rhamnegin. From solution in strong sulphuric acid, it is precipitated by water in its original state. It is always obtained when yellow berries are boiled with water, and separates on cooling from the aqueous extract, as a bright lemon-coloured powder, which may be purified by washing with water, alcohol, and ether. In dyeing with yellow berries, it is the rhamnegin, and not the rhamnin, which fixes itself on the tissue. On the other hand, Schützenberger (*Zeitschr. f. Chem.* [2] iv. 668) finds, in accordance with Gellatly (v. 100) and in opposition to Lefort, that rhamnegin (Gellatly's rhamnin) boiled with very dilute sulphuric acid, yields a colourless saccharine substance isomeric with mannite, $C^6H^{14}O^6$. The insoluble colouring matter obtained together with the sugar is not identical with quercetin, as Bolley supposes, but has the composition $C^{12}H^{10}O^5$, its formation being represented by the equation:

$$\underset{\text{Rhamnegin.}}{2C^{12}H^{16}O^7} + 3H^2O = \underset{\text{Rhamnetin.}}{C^{12}H^{10}O^5} + \underset{\text{Sugar.}}{2C^6H^{14}O^6}$$

alcohol; melts at 159°, and resolidifies at 153°. It dissolves in strong sulphuric acid, forming a liquid of a splendid purple colour, and becoming red with a purple tinge when mixed with a considerable quantity of the concentrated acid; on addition of water this colour disappears, and a crystalline precipitate separates, which appears to consist of unaltered phenylene sulphide. With strong nitric acid it yields a crystalline substance, probably a nitro-substitution product.

PHENYLENE SULPHOBROMIDE, $C^6H^4SBr^2$, is produced by the action of bromine-vapour on phenylene sulphide, or more easily by adding bromine in slight excess to a cold-saturated solution of the sulphide in anhydrous carbon bisulphide, the compound then separating in small black prisms, which may be purified by washing with cold carbon bisulphide, and freed from that liquid by placing them under an air-pump receiver, exhausting, readmitting the air, and repeating these operations several times. The sulphobromide slowly gives up its bromine when exposed to dry air, and is quickly decomposed by moisture, with evolution of hydrobromic acid. It is moderately soluble in carbon bisulphide and in carbon tetrachloride (Stenhouse, *loc. cit.*).

PHENYLENE-DIAMINE. $C^6H^8N^2 = \left.\begin{matrix}(C^6H^4)''\\ H^4\end{matrix}\right\}N^2$ (iv. 480).—The hydriodides of α and β phenylene-diamine are formed by the action of hydriodic acid on the corresponding nitranilines, the reduction of the α nitraniline appearing to require a somewhat higher temperature than that of β nitraniline. The α hydriodide is easily soluble, and crystallises in indistinct laminæ; the β salt is but slightly soluble, and crystallises in broad micaceous rectangular tables (Mills, *Chem. Soc. J.* [2] ii. 152).

Beta- or para-phenylene-diamine is formed, together with aniline, by heating amidazobenzene with tin and hydrochloric acid (Martius a. Griess, *Jahresb.* 1865, p. 419):

$$C^{12}H^9(NH^2)N^2 + 2H^2 = C^6H^8N^2 + C^6H^7N.$$

A double salt of phenylene-diamine hydrochloride and stannous chloride, $C^6H^8N^2.2HCl.2SnCl^2$, is formed by treating a mixture of dinitrobenzene (1 mol.) and metallic tin (6 at.) with strong hydrochloric acid. The whole dissolves with violent action, and the solution when left to evaporate deposits the double salt in needles having a silky lustre (H. Gerdemann, *Zeitschr. f. Chem.* [2] i. 51).

When nitrous acid is passed into the aqueous solution of phenylene-diamine hydrochloride, nitrogen is evolved, and a dark violet body, $C^{12}H^{10}N^4O^3$, is formed, slightly soluble in water, alcohol, and ether. This body slowly gives off nitrogen when treated with hydrochloric acid, and yields aniline hydrochloride when boiled with tin and hydrochloric acid. An acidulated solution of phenylene-diamine hydrochloride gives with potassium nitrite a brown amorphous precipitate (Hollemann, *ibid.* 555).

Dibromophenylene-diamine, $C^6H^6Br^2N^2$, is obtained as a dark brown precipitate on mixing the hydrochloride of phenylene-diamine with bromine till the odour of the latter remains permanent after some hours. It is nearly insoluble in ether, but dissolves easily in alcohol, and crystallises therefrom; cannot be sublimed without decomposition (Hollemann).

PHENYL-HYPOSULPHUROUS ACID. $C^6H^6S^2O^3$ (Stenhouse, *Proc. Roy. Soc.* xvii. 62; *Ann. Ch. Pharm.* cxlix. 254).—This acid is formed by dissolving phenyl sulphide $(C^6H^5)^2S$, with aid of heat in strong sulphuric acid. On dissolving the semi-solid mass which forms on cooling in a large quantity of water, neutralising with barium carbonate, evaporating the filtrate till a crystalline film forms on its surface, and then leaving it to cool, *barium phenylhyposulphite*, $(C^6H^5S^2O^3)^2Ba + 2H^2O$, separates in crusts composed of microscopic crystals. The copper salt also forms crystalline crusts. The calcium and sodium salts do not crystallise so well as the barium salt.

PHENYL-SULPHURIC ACID. $C^6H^6SO^4$ (Kekulé, *Zeitschr. f. Chem.* [2] iii. 641; *Jahresb.* 1867, p. 637).—Two modifications of this acid, which may be distinguished as α and β, are produced by dissolving phenol at a gentle heat in an equal weight of strong sulphuric acid; on diluting the product with water, neutralising with lead carbonate, decomposing the lead salts with hydrogen sulphide, neutralising the acid filtrate with potassium carbonate, and evaporating, potassium α phenylsulphate crystallises out first in six-sided anhydrous laminæ, while the β phenylsulphate is obtained from the mother-liquor in needles containing 2 mol. water. These two potassium salts, when fused with excess of potash, yield different modifications of oxyphenol, $C^6H^6O^2$, the α salt yielding resorcin, and the β salt pyrocatechin:

$$C^6H^5SO^4K + KHO = SO^3K^2 + C^6H^6O^2.$$

232°, a portion subliming in small white prisms, especially in a stream of gas. Its solutions in weak acids, not in excess, are colourless; those in somewhat stronger acids, especially in hydrochloric and sulphuric acids, have a purple-red colour. The coloration, which disappears on addition of alkalis, and is restored by acids, is so intense that 1 pt. of the base will colour 10,000 pts. of water purple-red, 200,000 pts. deep rose-red, and 800,000 pts. still distinctly red, although only 5 p. c. of the base is converted into the colouring substance. The colourless solution of rhœadine in acids is precipitated by tannic acid, and by mercuric, auric, and platinic chloride. The *platinum salt* has the composition $2(C^{21}H^{21}NO^6.HCl).PtCl^4 + 2H^2O$. The *hydriodide*, $C^{21}H^{21}NO^6.HI + 2H^2O$, separates on adding potassium iodide to a solution of the acetate, as a dense crystalline mass, consisting of small microscopic prisms, which give off half their water over sulphuric acid, the rest at 120°. The aqueous solution becomes red by prolonged boiling, part of the rhœadine being converted into rhœagenine; and on adding a drop of hydrochloric or sulphuric acid, the whole of the base is decomposed, the solution acquiring a purple-red colour. Cold dilute sulphuric acid converts rhœadine into a colourless resinous mass, which soon dissolves with splendid purple colour; on boiling the solution, it becomes dark purple, and on cooling deposits small prisms, brown-red by transmitted, green by reflected light, the liquid retaining rhœagenine amounting to 99 p. c. of the rhœadine, together with the colouring matter.

Opium contains a base different from rhœadine, but giving the same colour-reaction with sulphuric acid.

RHŒAGENINE. A base isomeric with rhœadine, and formed from it by the action of dilute mineral acids; it does not occur ready-formed in the poppy. When precipitated by ammonia from the solution, decolorised by animal charcoal, and recrystallised from alcohol, it forms small white prisms or laminæ, slightly soluble in ether, alcohol, water, and ammonia, easily and without colour in acids. The alcoholic solution blues reddened litmus. The base melts at 223°, but is not sublimable. The salts have a bitter taste, and some of them crystallise well. The *sulphate* is very soluble in water, and dries up to a varnish; its solution is precipitated by potassium dichromate, potassio-mercuric iodide, mercuric chloride, and acid platinic chloride. The *hydrochloride* forms concentrically grouped needles, easily soluble in water and in alcohol, precipitated from the aqueous solution by common salt. The *platinochloride* contains $2(C^{21}H^{21}NO^6.HCl).PtCl^4$. The *hydriodide*, $C^{21}H^{21}NO^6.HI$, forms short heavy prisms, moderately soluble in boiling, sparingly in cold water, nearly insoluble in aqueous potassium iodide. The *nitrate* forms vitreous prisms, slightly soluble in cold water, melting and partly dissolving in boiling water. The acetate crystallises in thin prisms.

RHUBARB. The portion of the aqueous extract of rhubarb-root which is soluble in alcohol contains, according to Kubly (*Chem. Centr.* 1867, p. 1056), the following constituents: 1. *Rheotannic acid*, $C^{26}H^{26}O^{14}$, precipitated (together with phæoretin) by lead acetate, and extracted by water after decomposition of the precipitate by hydrogen sulphide. It is a yellow-brown powder, insoluble in ether, but soluble in alcohol and in water; the brown, acid, aqueous solution precipitates organic bases white, ferric salts black-green, lead acetate and ferrous salts whitish-grey, but forms no precipitate with tartar-emetic. The lead precipitate contains $C^{26}H^{26}O^{14}.2PbO$. By boiling with acids or alkalis, rheotannic acid is resolved into fermentable sugar and red-brown amorphous *rheic acid*, $C^{20}H^{16}O^9$, which behaves with reagents like rheotannic acid.—2. *Phæoretin*, $C^{16}H^{16}O^7$, extracted by hot alcohol from the lead sulphide obtained in the preparation of rheotannic acid; *it has* essentially the properties described by Schlossberger a. Döpping (iv. 387). When the liquid filtered from the lead salt of rheotannic acid is freed from excess of lead by hydrogen sulphide, the resulting lead sulphide yields to water a large quantity of sugar, and to alcohol the following substances: 3. An indifferent substance, $C^5H^6O^2$, crystallising in prisms, insoluble in ether, slightly soluble in hot alcohol and water, and precipitated by lead acetate.—4. An orange-coloured bitter substance, designated by Kubly as *chrysophane*, which is insoluble in ether, but soluble in water and in alcohol, and decomposed by acids, with formation of sugar and flocculent chrysophanic acid.

RHUS. According to Maisch (*Chem. News*, xiii. 112), the poisonous principle of *Rhus Toxicodendron* is not a volatile base, as stated by Khittel (v. 109), but a volatile acid (*toxicodendronic acid*), which differs from formic acid by the circumstance that its sparingly soluble mercurous salt is not reduced by boiling. In the state of vapour or in aqueous solution it produces blisters and eruptions on the skin.

RHYOLITE. A rock occurring in trachytic and basaltic formations. For analyses, see *Jahresb.* 1865, p. 916; 1866, pp. 969, 976.

RICHMONDITE. This name is proposed by Kenngott (*Jahrb. Min.* 1866, p. 829) for the aluminium phosphate hitherto designated as *Gibbsite* (ii. 838).

RICINELAÏDIC ACID. $C^{18}H^{34}O^3$ (Ulrich, *Bull. Soc. Chim.* [2] ix. 225; *Jahresb.* 1867, p. 408).—This acid may be prepared by heating ricinoleic acid with pure nitric acid till red vapours are evolved, quickly cooling the product in cold water, pressing the solidified acid, and recrystallising it from hot alcohol. It crystallises in tufts of soft needles melting at 50°. It unites directly with bromine, forming oily *Ricinelaïdic dibromide*, $C^{18}H^{34}O^3Br^2$, which is converted by potash-ley even at ordinary temperatures into *Monobromoricinelaïdic acid*, $C^{18}H^{33}BrO^3$. This latter acid heated with alcoholic potash forms, together with potassium bromide, a solid acid different from ricinostearolic acid, melting at 71°, and crystallising from alcohol in short needles.

RICINOLEIC ACID. $C^{18}H^{34}O^3$ (Ulrich, *loc. cit.*).—By treating this acid at ordinary temperatures with 2 mol. phosphorus pentachloride, there is formed, according to the equation,

$$C^{18}H^{34}O^3 + 2PCl^5 = 2POCl^3 + 2HCl + C^{18}H^{32}Cl^2O,$$

a heavy oil, which is slowly decomposed by water, yielding a mobile, pungent liquid, floating on water, and having the composition $C^{18}H^{33}ClO^2$. This oil treated with alcoholic potash, but not with sodium-amalgam, yields a viscid oil, nearly free from chlorine, and exhibiting the characters of ricinoleic acid.

Ricinoleic dibromide, $C^{18}H^{34}O^3Br^2$, produced by gradually mixing cooled ricinoleic acid with 1 mol. bromine, and purified by saponification with weak potash-ley, is a heavy oil, colourless at first, but afterwards turning brown, insoluble in water, easily soluble in alcohol and ether. The potassium and ammonium salts are slightly soluble in water, easily in alcohol; the other salts are viscid glutinous masses.

Monobromoricinoleic acid, $C^{18}H^{33}BrO^3$, is formed by treating the dibromide with an alcoholic solution of 2 mol. potassium hydrate, and separates, on addition of hydrochloric acid, as a clear yellowish oil, not decomposing at 100°, easily soluble in alcohol and ether, forming with potash and ammonia, soaps slightly soluble in water. Mixed in a cooled vessel with 1 mol. bromine, it forms a yellowish, viscid, easily decomposible oil—probably *monobromoricinoleic dibromide*—which is quickly reconverted by alcoholic potash into monobromoricinoleic acid.

RICINOSTEAROLIC ACID, $C^{18}H^{32}O^3$, produced by heating monobromoricinoleic acid to 80° for about 8 hours with 2 mol. bromine, and purified by recrystallisation from alcohol, forms tufts or nodular groups of colourless needles, easily soluble in alcohol and ether, volatilising without decomposition, easily saponified by alkalis. The *ammonium salt* crystallises in slender needles, easily soluble in water, and gradually giving off all its ammonia on boiling; the *potassium salt*, which is likewise easily soluble, crystallises in slender needles or as a laminar mass; the *barium salt*, $(C^{18}H^{31}O^3)^2Ba$, is a precipitate insoluble in ether, crystallising from alcohol in laminæ which melt at 135°; the *silver salt*, $C^{18}H^{31}O^3Ag$, is a granular precipitate gradually decomposed by hot alcohol (Ulrich, *loc. cit.*).

Ricinostearolic dibromide, $C^{18}H^{32}O^3Br^2$, is formed as a thickish, yellowish oil, on gradually mixing cooled ricinostearolic acid with 1 mol. bromine. In contact with excess of bromine, it is converted into the *tetrabromide* $C^{18}H^{32}O^3Br^4$, a heavy, easily decomposible oil. The dibromide is decomposed by alcoholic potash at 150° (the tetrabromide at ordinary temperatures), yielding ricinostearolic acid smelling of octyl alcohol.

RICINOSTEAROXYLIC ACID, $C^{18}H^{32}O^4$, is obtained by prolonged heating of ricinostearolic acid with 1½ pt. recently precipitated silver oxide, decomposing the resulting silver salt with hydrochloric acid, and recrystallising the acid extracted by ether. It crystallises from alcohol in dendritic groups of needles, melts at 78°, solidifies to a hard alabaster-like mass, and is easily saponified by alkalis. The *ammonium salt* crystallises in ring-shaped groups of needles soluble in alcohol; the *silver salt*, $C^{18}H^{31}O^4Ag$, is a granular precipitate decomposed by hot alcohol; the *barium salt*, $(C^{18}H^{31}O^4)^2Ba$, separates from alcoholic solution as a jelly. Ricinostearoxylic acid is distinguished from the isomeric compound, stearoxylic acid, by not uniting with bromine without evolution of gas. When ricinoleic dibromide is heated to 100° with silver oxide and water, there is formed, together with octylic alcohol, a mass which, when decomposed by hydrochloric acid, yields to ether a yellow rancid-smelling oil, which deposits ricinostearoxylic acid melting at 78° (Ulrich, *loc. cit.*).

ROCHELLA. See ORCHELLA-WEEDS.

ROSANILINE. The salts of this base heated to 18° with potash in al solution yield a yellowish liquid from which water throws down free rosan coloured deep yellow by admixture of chrysaniline, as is also the wash-water; exposure to air and light, the precipitate turns orange-red, and the wash-wa sunshine turns blue. *Rosatoluidine salts* similarly treated also yield a ye liquid, from which water throws down the base in faintly reddish flocks, b precipitate and the wash-water becoming violet when exposed to sunshine. R toluidine salts heated to 280° for several days with glycerin and a little alco a red liquid which is precipitated by ammonia, but not by water; the precip dark violet, the wash-water light violet. Rosaniline salts similarly treated y red-brown precipitate and a yellow-brown wash-water. Rosaniline salts ar soluble than rosatoluidine salts, and the free base is more easily separated fr former than from the latter by alkalis. The solutions of rosaniline salts dyeing exhibit a faint yellowish reflex; those of rosatoluidine do not. The power of rosaniline salts is to that of rosatoluidine salts as 100° to 140° (A. Ros *Bull. Soc. Chim.* [2] vi. 354).

On the reaction of the *camphene hydrochlorides*, $C^{10}H^{16}.HCl$ and $C^{10}H^{16}.2HC$ rosaniline, see TERPENES.

Action of Aldehydes on Rosaniline.—When the yellow solution of rosaniline (or other salt) in aqueous sulphurous acid is mixed with a few drops of an al (bitter almond oil, œnanthol, or valeral), the rosaniline being kept in excess, sulp anhydride is given off, the solution turns red and afterwards violet, and gr deposits copper-coloured crystalline scales consisting of the mono-acid salts following bases:

Benzylidene-rosaniline | Heptylidene-rosaniline | Amylidene-rosaniline

$$\left.\begin{matrix}C^{20}H^{16}\\C^7H^6\\H\end{matrix}\right\}N^3 \qquad \left.\begin{matrix}C^{20}H^{16}\\C^7H^{14}\\H\end{matrix}\right\}N^3 \qquad \left.\begin{matrix}C^{20}H^{16}\\C^5H^{10}\\H\end{matrix}\right\}N^3.$$

These bases do not form triacid salts. The copper-coloured *arsenate of h lidene-rosaniline* consists of $C^{27}H^{31}N^3.AsHO^3$; the yellow *platinochlori* $C^{27}H^{31}N^3.2HCl.PtCl^4$. By acting upon these bases in alcoholic solution with iodide (or with iodine and phosphorus) the typic hydrogen-atom may be replac ethyl. The salts of the ethylated bases are insoluble in ether, water, and dilute a but dissolve easily in alcohol, forming violet solutions (Schiff, *Bull. Soc. Chi* vii. 518).

Œnanthol forms with crystallised rosaniline acetate, even at ordinary tempera a compound which dissolves in alcohol with blue colour, and yields with caustic p red crystalline flocks of *triheptylidene-dirosaniline*, $C^{61}H^{71}N^6$:

$$\underset{\text{Rosaniline.}}{2(C^{20}H^{16})^{vi}H^3N^3} + \underset{\text{Œnanthol.}}{3C^7H^{14}O} = 3H^2O + \underset{\text{Triheptylidene-rosaniline.}}{(C^{20}H^{16})^{vi}(C^7H^{14})^3N^6}$$

This base, as well as its salts, decomposes below 100°, especially in presence of ex of œnanthol, forming a yellow resinous mass composed for the most part of *hepty ditoluidene-diamine*, $(C^7H^{14})(C^7H^6)^2N^2$. The decomposition in presence of œnan may perhaps be represented by the following equation:

$$2\left[\left.\begin{matrix}C^6H^4\\(C^7H^6)^2\\H^3\end{matrix}\right\}N^3\right] + 3C^7H^{14}O = \left.\begin{matrix}(C^6H^4)^2\\C^7H^{14}\end{matrix}\right\}N^2 = 2\left[\left.\begin{matrix}(C^7H^6)^2\\C^7H^{14}\end{matrix}\right\}N^2\right] + 3H^2O$$

Rosaniline. | Œnanthol. | Heptylidene-diphenylene-diamine. | Heptylidene-ditoluidene-diamine.

The formation of heptylidene-diphenylene-diamine has not however been distin proved; it has merely been observed that the heptylidene-ditoluidene-diamine accompanied by another base of lower boiling point. *Benzoic aldehyde* forms w rosaniline at 90°–100° a violet mass, which, from the analysis of its platinum s appears to contain *toluidine-rosaniline*, $[(C^{20}H^{16})(C^7H^6)H]N^3$; at 120° a crystalli copper-red product is formed; and at 150°–160°, with excess of benzoic aldehyde there is obtained a heavy yellow oil from which alcohol separates a sandy powder (Schiff, *Bull. Soc. Chim.* [2] v. 291).

Hydrocyan-rosaniline. $C^{20}H^{19}N^3.HCy$ (v. 115).

ROSE OIL. The camphor or stearoptene of this oil (obtained from roses grown at Mitcham), when carefully fused by the heat of the sun, solidifies on cooling, in microscopic, truncated, six-sided pyramids, not belonging to the rhombohedral system. It has the composition of an olefine, C^nH^{2n}, melts at 32·5, gives off vapours at 150°, begins to boil at 272°, boils completely at 275°, turns brown and black at 300°. When oxidised by fuming nitric acid, it yields succinic acid, together with a small quantity of oxalic acid, and perhaps valeric and formic acids. A mixture of potassium chromate and sulphuric acid produces no perceptible effect upon it, beyond the emission of a faint odour of acrolein (Flückiger, *Zeitschr. f. Chem.* [2] vi. 126).

ROSOCYANIN. See CURCUMIN.

ROSOLIC ACID. $C^{20}H^{16}O^3$ or $C^{20}H^{18}O^4$.—The formation of this acid from rosaniline by the action of nitrous acid has already been noticed (v. 584). The equations representing it are as follows:

$$\underset{\text{Rosaniline.}}{C^{20}H^{19}N^3} + 3HNO^2 = \underset{\text{Azorosaniline.}}{C^{20}H^{10}N^6} + 6H^2O.$$

$$\underset{\text{Azorosaniline.}}{C^{20}H^{10}N^6} + 3H^2O = \underset{\text{Rosolic acid.}}{C^{20}H^{16}O^3} + 3N^2.$$

The deep red solution of rosaniline turns brown when mixed with excess of hydrochloric acid, then yellow when nitrous acid is passed into it, and deposits on boiling a dark-coloured solid body which differs from rosolic acid obtained from phenol (by the action of sulphuric acid on a mixture of phenol and oxalic acid) in this respect, that its salts are not coloured darker by potassium ferricyanide. It seems probable that the rosolic acid obtained from phenol may contain a body (likewise produced from leucaniline, and therefore called *leucorosolic acid*) which induces the darker coloration by the ferricyanide. The same body is formed by the reducing action of zinc and hydrochloric acid on rosolic acid obtained from rosaniline; and, on the other hand, rosolic acid from phenol, after treatment with potassium ferricyanide, precipitation with acid, and solution in alkali, exhibits exactly the same characters as that which is produced from rosaniline (Wanklyn a. Caro, *Proc. Roy. Soc.* xv. 210).

Caro (*Phil. Mag.* [4] xxxii. 126) has also endeavoured to determine whether the formation of rosolic acid from phenol requires the presence of a substance which, like cresol, oxalic acid, &c., contains carbon in the form in which it exists in the fatty series. He finds that (similarly to the formation of rosaniline) pure phenol or pure cresol treated with manganese dioxide, mercuric sulphate, arsenic anhydride, or iodine, does not yield a trace of rosolic acid. This acid is however always formed when a mixture of phenol and cresol is employed; also from pure phenol (but not from cresol) heated with strong sulphuric acid and oxalic acid, with sulphuric acid and amyl iodide, with bromacetic acid, with acetic acid and iodine, with formates and iodine, and in considerable quantity with iodoform. In a similar manner rosaniline is produced from pure aniline (free from toluidine) by heating with iodoform or with lead formate and iodine, and in smaller quantity by the action of chloroform, carbon chloride, or cyanogen iodide. With toluidine there is formed under the same circumstances a brown product not containing rosaniline. Hence Caro concludes that in rosolic acid, as in rosaniline, part of the carbon is combined in the same manner as in the aromatic bodies, part as in the fatty bodies, as indicated by the following equations of formation:

$$\begin{array}{lclcl} \text{Aniline} & & \text{Toluidine} & & \text{Rosaniline} \\ C^6H^5(NH^2) & + & 2[C^6H^4(CH^3)(NH^2)] & = & C^{20}H^{19}N^3 + 3H^2 \\ 3[C^6H^5(NH^2)] & + & 2C & = & C^{20}H^{19}N^3 + H^2 \end{array}$$

$$\begin{array}{lclcl} \text{Phenol} & & \text{Cresol} & & \text{Rosolic acid} \\ C^6H^5(OH) & + & 2[C^6H^4(CH^3)(OH)] & = & C^{20}H^{16}O^3 + 3H^2 \\ 3[C^6H^5(OH)] & + & 2C & = & C^{20}H^{16}O^3 + H^2 \end{array}$$

RUFIGALLIC ACID. The crystalline grains of this acid obtained by treating dry gallic acid with strong sulphuric acid (v. 133) are anhydrous, and have the composition $C^7H^4O^4$; they have the colour of carmine, and appear under the microscope as acute rhombohedrons. The amorphous acid $C^7H^4O^4.H^2O$ * gives off its water (10·58 p. c.) at 135°. The acid may be sublimed in cinnabar-red prismatic crystals, which do not lose weight at 125°. It is insoluble in cold, slightly soluble in boiling water, also in alcohol and ether; in potash and ammonia it dissolves with red colour when the air is excluded, with brown colour in contact with air; the alcoholic solution is neutral. It does not yield pyrogallic acid when heated with potash or lime. Baryta-water does not dissolve it, but converts it into an indigo-blue mass soluble in potash (Wagner, *Chem. Centr.* 1861, p. 47). By fusion with potash it is converted into oxyquinone, $C^6H^4O^3$ (Malin, p. 893).

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* Misprinted $C^6H^4O^4$ in vol. v. p. 13.

According to Löwe (*J. pr. Chem.* cvii. 296; *Zeitschr. f. Chem.* [2] vi. 128), the formula of rufigallic acid is $C^{14}H^8O^8$, and its formation from gallic acid is attended with the formation of a product of oxidation, the oxygen being supplied at the expense of the sulphuric acid: other dehydrating agents, zinc chloride for example, do not convert gallic into rufigallic acid. By strong potash solution, and especially by alcoholic potash, it is converted into a blue-black salt.

RUTIN. According to Spiess a. Sostmann (*Jahresb.* 1865, p. 587), this substance, $C^{25}H^{32}O^{17}$ (or $C^{25}H^{28}O^{15}$ $2H^2O$), is easily obtained from commercial Chinese yellow berries in grains (the undeveloped flower-buds of *Sophora japonica*, known as Waifa), whereas Chinese yellow berries in pods (the fruit of *Gardenia radicans* and *G. florida*) contain, not rutin, but mannite.

S

SACCHARIC ETHER. Crystallised ethyl saccharate gently heated with 4 mol. acetyl chloride, is converted into a crystalline compound, $C^{10}H^{10}O^8$, mixed with an oil insoluble in water. The crystalline body is perhaps formed in the manner shown by the equation:

$$\underset{\text{Saccharic acid.}}{C^6H^{10}O^8} + \underset{\text{Acetyl chloride.}}{4C^2H^3OCl} = \underset{\text{Crystalline compound.}}{C^{10}H^{10}O^8} + \underset{\text{Acetic acid.}}{2C^2H^4O^2} + 4HCl.$$

When the crystalline compound of ethyl saccharate and calcium chloride is heated to 100° with somewhat more than an equal weight of acetyl chloride, a gummy mass is formed which gives up to anhydrous ether an oil easily soluble in water and alcohol, and solidifying for the most part in the crystalline form over sulphuric acid. The crystals consist of *ethylic tetracetyl-saccharate*, $C^6H^4(C^2H^3O)^4O^8.(C^2H^5)^2$. This ether crystallises from alcohol in monoclinic prisms, melting at 61°, insoluble in water, soluble in alcohol and ether, and resinised by alcoholic potash (Baltzer, *Bull. Soc. Chim.* [2] x. 263).

SAFFRON (B. Weiss, *J. pr. Chem.* ci. 65).—When dried saffron, after exhaustion with ether, which removes a small quantity of a yellowish oil, is digested with water, gum, vegetable mucilage, inorganic salts, and sugar are dissolved, together with the unaltered colouring matter of the saffron; from this solution, the gum, mucilage, and inorganic salts may be precipitated by absolute alcohol; and the filtrate mixed with ether deposits the colouring matter mixed with small quantities of sugar and salts. This colouring matter, polychroïte, $C^{48}H^{60}O^{18}$ (?), forms an orange-yellow precipitate which dries up over sulphuric acid to a friable, ruby-coloured, deliquescent mass. It is inodorous, has a faint, sweetish taste, dissolves easily in water and in dilute alcohol, but is nearly insoluble in absolute alcohol. The aqueous solution is turned brown by hydrogen sulphide, and is decolorised by nitrous acid or chlorine. By dilute acids it is resolved into a red secondary colouring matter (crocin), sugar, and an aromatic oil having the characteristic odour of saffron. On heating its aqueous solution with dilute sulphuric acid (not in excess) in a retort through which a stream of hydrogen is passed, crocin separates as a red powder, while the oil distils over.

Crocin has the composition $C^{16}H^{18}O^6$; an orange-yellow lead salt precipitated from its alcoholic solution by lead acetate contains $(C^{16}H^{17}O^6)^2Pb$; a red substance very much like crocin, left undissolved by ether in the preparation of polychroïte, consists of $2C^{16}H^{18}O^6.3H^2O$. Crocin dissolves very sparingly in water, easily in alcohol and in dilute alkalis. From the alcoholic solution it is precipitated by ether, from solution in alkalis by acids, in purple-red flocks. Heated with strong potash-ley, it decomposes, with evolution of pungent vapours. With strong sulphuric acid it acquires a deep blue colour, gradually changing to violet and brown; nitric acid colours it green, changing to yellow-brown. Crocin suspended in water dissolves in nitric acid to a colourless liquid, without formation of oxalic acid; it is decolorised by chlorine; not affected by sulphurous acid.

The mobile *volatile oil* obtained in the decomposition of polychroïte is yellow, has the odour of saffron, and boils at 208°–210°. It mixes in all proportions with alcohol and ether, is insoluble in water, but is decomposed by prolonged contact with it, the liquid acquiring an acid reaction and becoming covered with white films. Heated with potash-ley it decomposes, giving off pungent vapours; alcoholic potash converts it into a resin. It quickly reduces silver solution, especially on addition of ammonia; is coloured brown by solution of iodine in potassium iodide; does not unite with alkaline bisulphites.

The decomposition of polychroïte by acids appears to take place in the manner represented by the equation:

$$\underset{\text{Polychroïte.}}{C^{48}H^{60}O^{18}} + H^2O = \underset{\text{Crocin.}}{2C^{16}H^{18}O^6} + \underset{\text{Oil.}}{C^{10}H^{14}O} + \underset{\text{Sugar.}}{C^6H^{12}O^6}$$

SAFRENE and **SAFROL.** See SASSAFRAS OIL.

SALAMANDRINE. $C^{34}H^{60}N^2O^5$.—An alkaloïd obtained from the poisonous secretion of the cutaneous glands of the land salamander (*Salamandra maculata*). It is not volatile, crystallises with water, dissolves easily in water and in alcohol, and has an alkaline reaction. The *hydrochloride*, $C^{34}H^{60}N^2O^5.2HCl$, crystallises in needles, but becomes amorphous in drying (Zalesky, *Bull. Soc. Chim.* [2] vi. 344; *Jahresb.* 1866, p. 755).

SALEP. The orchis-roots known by this name contain, according to Dragendorff (*Jahresb.* 1865, p. 633), 48·1 p. c. dextrin, arabin, and semi-soluble vegetable mucilage, 27·3 starch, 1·2 sugar, 2·4 cellulose, 4·9 proteids, and 4·8 p. c. ash (containing 28·8 p. c. phosphoric anhydride, and 23 p. c. potash).

SALHYDRANILIDE.
SALHYDRETHANILIDE. } See SALICYLOL, AMIDES OF (p. 1011).

SALICIN. $C^{13}H^{18}O^7$. This compound is not decomposed by water in closed vessels, either at ordinary temperatures or at 100°; but in contact with the air the aqueous solution is soon found to contain sugar and saligenin, at the same time that mould forms on its surface. If this mould be introduced into a salicin-solution kept from contact with the air, the resolution of the salicin into sugar and saligenin takes place more quickly (Moitessier, *Jahresb.* 1866, p. 676).

Salicin dissolves in a solution of sodium in alcohol, the liquid after a while solidifying to a crystalline pulp, which when washed with alcohol and dried at a gentle heat yields a white brittle mass of *sodium-salicin*, $C^{13}H^{17}NaO^7$ (Perkin, *Chem. News*, xviii. 110).

Bromosalicin, $C^{13}H^{17}BrO^7$, is formed by gradually adding bromine to a solution of salicin in 20 pts. water. The liquid then solidifies to a pulp, which, when freed by ether from a resinous substance, crystallises from water in four-sided prisms of hydrated bromosalicin, $C^{13}H^{17}BrO^7.2H^2O$. This compound tastes bitter, like salicin, is easily soluble in water and alcohol, insoluble in ether, gives off its water at 110°, melts at 160°, and decomposes at about 200°. Bromosalicin is decomposed by emulsin, less easily than salicin; the bromosaligenin thereby produced forms a blue colour with ferric chloride, like saligenin. Acids added to its solution throw down bromosaliretin. Its aqueous solution is precipitated by basic lead acetate. Bromosalicin treated in warm solution with excess of bromine, is converted into a pulverulent compound containing 25·28 p. c. bromine (O. Schmidt, *Zeitschr. f. Chem.* [2] i. 320).

Derivatives of Salicin containing Acid Organic Radicles.—Salicin treated at ordinary temperatures with acetyl chloride is converted into a compound of acetyl chloride with tetracetyl-salicin:

$$C^{13}H^{18}O^7 + 5C^2H^3OCl = 4HCl + C^{13}H^{14}(C^2H^3O)^4O^7.C^2H^3OCl.$$

This compound is insoluble in water, slightly soluble in ether, easily soluble in alcohol, from which it is deposited in small crystals. By hot dilute mineral acids it is resolved into sugar, saliretin, acetic acid, and hydrochloric acid; by alkalis into salicin and the same acids; with silver nitrate it yields tetracetyl-salicin, acetic acid, and silver chloride. *Tetracetyl-salicin* is soluble in water, alcohol, and ether, crystallises in needles, and reacts with acids and alkalis in the manner just mentioned: it is not decomposed by emulsin. The chlorides of butyryl, valeryl, and caproyl yield with salicin uncrystallisable products, and the lead-compound of salicin heated to 100° with ethyl iodide yields only a resinous body. Monochlorosalicin is converted by acetyl chloride into *acetochlorosalicin*, $C^{13}H^{16}Cl(C^2H^3O)O^7$, which crystallises from alcohol, and reacts like tetracetyl-salicin (Moitessier, *loc. cit.*).

According to Schiff (*Zeitschr. f. Chem.* [2] v. 51), tetracetyl-salicin may be obtained directly by treating salicin with a large excess of acetyl chloride at a rather low temperature in an open vessel, care being taken to remove the hydrochloric acid formed at the same time as quickly as possible. Salicin treated in the same manner with benzoyl chloride, is converted into *benzoyl-salicin* or populin, $C^{13}H^{17}(C^7H^5O)O^7$. Schiff has also obtained *di-* and *tri-benzoyl salicin*. Both these compounds are insoluble in hot water; in ether, tetrabenzoyl-salicin dissolves very easily, dibenzoyl-salicin scarcely at all. Tetrabenzoyl-salicin is a colourless resin, which when boiled with hydrochloric acid yields a large quantity of benzoic acid, together with saliretin and a humus-like compound of glucose.

Schiff represents salicin and its tetracetyl derivative by the following formulæ:

$$C^6H^7\left\{\begin{matrix}O\\(OH)^4\end{matrix}\right. \qquad\qquad C^6H^7\left\{\begin{matrix}O\\(OC^2H^3O)^4\end{matrix}\right.$$

$$C^6H^4\left\{\begin{matrix}O\\CH^2.OH\end{matrix}\right. \qquad\qquad C^6H^4\left\{\begin{matrix}O\\CH^2.OH\end{matrix}\right.$$

Salicin (Glycosalicyl alcohol). Tetracetyl-salicin.

SALICYLAMIDE. $C^7H^7NO^2 = C^6H^4\left\{\begin{matrix}OH\\CONH^2\end{matrix}\right.$—This compound, produced by the action of ammonia on acid methyl salicylate (winter-green oil), is sometimes called salicylamic acid (v. 150), but its mode of formation shows it to be salicylamide analogous in constitution to glycollamide:

$$\underset{\text{Acid methyl salicylate.}}{C^6H^4\left\{\begin{matrix}OH\\CO(OCH^3)\end{matrix}\right.} + NH^3 = \underset{\text{Methyl alcohol.}}{HOCH^3} + \underset{\text{Salicylamide.}}{C^6H^4\left\{\begin{matrix}OH\\CONH^2\end{matrix}\right.}$$

The true salicylamic acid, $C^6H^4\left\{\begin{matrix}NH^2\\COOH\end{matrix}\right.$, analogous to glycollamic acid, has not yet been obtained.

Salicylamide treated with phosphorus pentachloride is converted into *salicylo-chloronitrile*, $C^6H^4\left\{\begin{matrix}Cl\\CN\end{matrix}\right.$ (L. Henry, *Zeitschr. f. Chem.* [2] vi. 53).

Methyl-salicylamide, $C^6H^4\left\{\begin{matrix}OCH^3\\CONH^2\end{matrix}\right.$, is produced by the action of ammonia at 150° on methylic methyl-salicylate, $C^6H^3\left\{\begin{matrix}OCH^3\\COOCH^3\end{matrix}\right.$, and crystallises, by slow evaporation of its ethereal solution, in long shining prisms melting at 128°–129°. When heated to 150°, it does not yield a compound analogous to salicylonitrile (p. 1012), the greater portion distilling without decomposition (Grimaux, *Bull. Soc. Chim.* [2] xiii. 25).

SALICYLIC ACID. $C^7H^6O^3 = C^6H^4\left\{\begin{matrix}OH\\COOH\end{matrix}\right.$. *Metaoxybenzoic Acid.*—*Formation*: *a*. By heating phenol with acid potassium carbonate and a little water to 160° in a sealed tube (Drechsel, *Jahresb.* 1865, p. 367):

$$C^6H^6O + CO^3HK = H^2O + C^7H^5O^3K.$$

β. By the action of nitrous acid on meta-amidobenzoic acid (Hübner a. Petermann, *Ann. Ch. Pharm.* cxlix. 129):

$$C^7H^7NO^2 + NO^2H = C^7H^6O^3 + N^2 + H^2O.$$

γ. By heating monochlorotoluene with fuming sulphuric acid, whereby it is converted into chlorosulphobenzylic acid, $C^6H^4Cl.CH^2SO^3H$, and fusing the potassium salt of this acid with excess of potash. The chlorine and the sulphuric residue, SO^3H, are then replaced by hydroxyl, forming the compound $C^6H^4OH.CH^2OH$; and this, under the oxidising influence of the potash, is converted, with evolution of hydrogen, into potassium salicylate:

$$C^6H^4OH.CH^2OH + KHO = C^6H^4(OH).CO^2K + 2H^2.$$

The acid separated from this salt by hydrochloric acid agrees with salicylic acid in all its characteristic properties (Vogt, *Zeitschr. f. Chem.* [2] v. 577).—*δ*. When sodium in small pieces is added to a mixture of equal parts of ethyl chlorocarbonate and phenol, in sufficient quantity to combine with all the chlorine present, ethyl salicylate is formed, together with a very large quantity of phenyl-ethyl carbonate (Wilm a. Wischin, *ibid.* iv. 6).

Decomposition by Heat.—Salicylic acid heated alone or with water is resolved into phenol and carbon dioxide between 220° and 230°; but when it is heated with concentrated aqueous hydriodic or hydrochloric acid, or with dilute sulphuric acid (1 pt. acid to 3 pts. water) the decomposition takes place at 140°–150°, and the more quickly

Pyrophosphamates are formed by the action of metallic chlorides on the diamic acid, thus:

$$P^2(NH^2)^2H^2O^5 + H^2O + 3MCl = NH^4Cl + 2HCl + P^2(NH^2)M^3O^6.$$

Pyrophosphotriamic acid appears to be formed from an amidated oxychloride of unknown composition.

TETRAPHOSPHAMIC ACIDS (Gladstone, *Chem. Soc. J.* [2] vi. 261).—These acids, also produced by the action of water on the amides of phosphorus oxychloride, may be derived from tetraphosphoric acid, $P^4(HO)^6O^7$, the acid corresponding to the phosphates, $P^4(MO)^6O^7$ (iv. 537); thus:

Tetraphosphodiamic acid	$P^4(NH^2)^2(HO)^4O^7$.
Tetraphosphotetramic acid	$P^4(NH^2)^4(HO)^2O^7$.

When phosphorus oxychloride is saturated at a low or moderately high temperatures with ammonia, a white mass is formed which dissolves completely in water, with exception of a small quantity of pyrophosphotriamic acid; and alcohol added to this solution throws down either a viscid liquid or light solid precipitate, sometimes also a glutinous substance which appears to be a mixture of the other two. The liquid compound, when purified by washing with alcohol, repeated precipitation by alcohol from its aqueous solution, and drying in a vacuum, has the composition $P^4N^5H^{17}O^{11}$. It is very hygroscopic, sustains a temperature of 100° without decomposition, gives off ammonia when treated with cold potash-ley, and is decomposed by hydrochloric acid into orthophosphoric acid and sal-ammoniac. With ammonia it forms a liquid compound slightly soluble in water, insoluble in alcohol, from which the original substance is separated by dilute sulphuric acid. In aqueous solution it forms solid precipitates with many metallic salts, but appears at the same time to undergo alteration, inasmuch as neither of these compounds contains more than 3 at. nitrogen to 4 at. phosphorus, and they all, when decomposed by acids, yield solid tetramides and pyrophosphamic acids. From its reaction with potash, the compound $P^4N^5H^{17}O^{11}$ may be regarded as the triammonium salt of *tetraphosphodiamic acid*, $P^4(NH^2)^2H(NH^4)^3O^{11}$.

Tetraphosphotetramic acid, $P^4(NH^2)^4H^2O^9$, is obtained either by decomposing the liquid compound with a metallic salt, and the precipitate with an acid, or more readily by dissolving the above-mentioned glutinous body in water, decomposing it with a large excess of a mineral acid, precipitating with alcohol, and repeating this treatment till the precipitate becomes sparingly soluble in water, and friable after drying. It is likewise produced by boiling the liquid acid with water for several hours, or by treating it with alkalis or strong acids. Its formation is usually accompanied by that of pyrophosphodiamic or pyrophosphotriamic acid. It combines with bases, and is separated by acids from the resulting compounds, apparently unaltered. It appears to form two ammonium salts, one of which, precipitated by alcohol from the aqueous solution, has the composition $P^4(NH^2)^4H(NH^4)O^9$, and gives off all its ammonia in a vacuum. Two *silver salts*, $P^4N^4H^4Ag^6O^9$ and $P^4N^4H^8Ag^2O^9$, have also been examined.

Tetraphosphopentazotic Acid. $P^4N^5H^9O^7$.—When phosphorus oxychloride is rapidly saturated with ammonia, the mass becomes strongly heated, and when treated with water leaves a body different from pyrophosphotriamic acid. This compound is obtained in greater purity when the product, saturated with ammonia, is heated above 200°, but not to the volatilising point of sal-ammoniac, and then exhausted with water. The insoluble residue consists of tetraphosphopentazotic acid. It is decomposed with moderate facility by water, and quickly at the boiling heat, with formation of pyrophosphamic acids; a similar transformation takes place gradually in the dry state and at ordinary temperatures. The salts of this acid are nearly or quite insoluble. The ammonium salt, $P^4N^5H^8(NH^4)O^7$, and the potassium salt, $P^4N^5H^8KO^7$, have been examined; also the silver, copper, and lead salts, which, however, have not been obtained of constant composition.

When tetraphosphopentazotic acid is treated with neutral or slightly acidulated silver nitrate, a pale yellowish-brown precipitate is formed, having nearly the composition $P^4N^4H^4Ag^2O^7$. Gladstone regards this salt as the silver salt of *tetraphosphotetrimic acid*, $P^4(NH)^4H^2O^7$ (*Chem. Soc. J.* [2] vii. 22).

PHOSPHAMIDES. By passing dry ammonia gas into phosphorus oxychloride, and digesting the product with water to dissolve sal-ammoniac, Schiff (iv. 498) obtained phosphotriamide, $PO(NH^2)^3$. Gladstone, on the other hand, did not obtain this compound, but only the intermediate bodies $POCl^2(NH^2)$ and $POCl(NH^2)^2$ (*Chem. Soc. J.* [2] vii. 16). Schiff, however, in a recent paper (*Zeitschr. f. Chem.* [2] v. 609) again asserts the formation of the phosphotriamide, and points out that in gives off 1 mol. water at 100°, the rest at 150°. A *basic barium salt*, $2C^7H^2I^2O^3Ba + 3H^2O$, is obtained, like the corresponding mono-iodosalicylate, in small silky tables, dissolving very sparingly, but with strong reaction, in water, becoming anhydrous at 150°. The *calcium salt*, $(C^7H^3I^2O^3)^2Ca + 5H^2O$, separates from a boiling aqueous solution on cooling in highly lustrous neutral needles, soluble in 1160 pts. water at 18°, becoming anhydrous at 120° (Liechti).

Amidosalicylic or Meta-amidoxybenzoic acid, $C^7H^7NO^3 = C^6H^3(NH^2)\left\{\begin{matrix}OH\\ CO^2H\end{matrix}\right.$ is produced by the action of tin and hydrochloric acid on nitrosalicylic acid (Beilstein, *Ann. Ch. Pharm.* cxxx. 242):

$$C^7H^5(NO^2)O^3 + 3Sn + 6HCl = C^7H^5(NH^2)O^3 + 2H^2O + 3SnCl^2;$$

also by heating the nitro-acid with fuming hydriodic acid and a little phosphorus to 120°–130°, and by treating the nitric acid with sodium-amalgam (Moitessier, *Jahresb.* 1865, 385); not by the action of ammonium sulphide (R. Schmitt, *Zeitschr. Ch. Pharm.* 1864, 321).

The liquid obtained by the first process solidifies to a crystalline pulp, consisting of a compound of stannous chloride with the hydrochloride of amidosalicylic acid, which, when dissolved in water, decomposed with hydrogen sulphide, and evaporated in a stream of that gas, yields colourless crystals of the hydrochloride; and this, when carefully neutralised in aqueous solution with caustic soda, yields a network of silky crystals of amidosalicylic acid. This acid is insoluble in cold water and in alcohol, sparingly soluble in hot water. Its hot aqueous solution exposed to the air quickly deposits a brown amorphous decomposition-product, which is likewise formed by the action of acids or alkalis. Ferric chloride first colours the solution deep cherry-red, and then forms a black-brown precipitate (more quickly on addition of chlorine or bromine).

The salts of amidosalicylic acid are permanent in the dry state, but very unstable in solution; those of the alkali-metals and alkaline-earth metals are easily soluble, crystallisable, and mostly black-brown; those of the heavy metals are sparingly soluble, easily decomposible precipitates (Schmitt).

Hydrochloride of Amidosalicylic acid, $C^7H^7NO^3.HCl$, crystallises in long needles, easily soluble in water and alcohol at the boiling heat. The solution, which decomposes even on exposure to air, deposits brown flocks on addition of auric or platinic chloride. The *hydriodide*, $C^7H^7NO^3.HI$, crystallises in yellowish needles or laminæ, more stable in solution than the hydrochloride. The *sulphate*, $2C^7H^7NO^3.SO^4H^2 + H^2O$, crystallises in slightly soluble colourless prisms (Schmitt).

Diamidosalicylic acid, $C^7H^8N^2O^3 = C^7H^4(NH^2)^2O^3$, is produced by the action of phosphorus iodide and water on methyl dinitrosalicylate (v. 164):

$$C^7H^3(NO^2)^2O^3.CH^3 + 13HI = C^7H^4(NH^2)^2O^3 + CH^3I + 4H^2O + 6I^2.$$

The resulting liquid, decolorised by phosphorus at the boiling heat and filtered from amorphous phosphorus, deposits on evaporation a crystalline mass of the hydriodide of diamidosalicylic acid; and on decomposing this compound in alcoholic solution with sodium carbonate not in excess, diamidosalicylic acid separates in colourless stellate groups of needles. It is insoluble in alcohol, but dissolves easily in hot water and in dilute acids, excepting acetic acid. The solutions quickly decompose in contact with the air, so that the acid becomes coloured even by recrystallisation from water. The aqueous solution is coloured brown-red by ferric chloride or nitrous acid, depositing black flocks after some time.

Hydriodide of diamidosalicylic acid, $C^7H^8N^2O^3.2HI + 1\frac{1}{2}H^2O$, is very soluble in water and alcohol, more stable in presence of free hydriodic acid than in neutral solution, and crystallises in faintly yellowish rhombic tables. The *hydrochloride*, $C^7H^8N^2O^3.2HCl$, forms square prisms easily soluble in water, less soluble in alcohol. The *sulphate*, $C^7H^8N^2O^3.SO^4H^2 + H^2O$, separates on adding sulphuric acid to an alcoholic solution of the hydriodide, in stellate groups of square prisms slightly soluble in water, nearly insoluble in alcohol. The *nitrate* has been obtained only in groups of black crystals (Saytzeff, *Ann. Ch. Pharm.* cxxxiii. 321).

Diazosalicylic acid, $C^7H^4N^2O^3$, separates on passing nitrous acid into an alcoholic solution of the hydrochloride of amidosalicylic acid, in slender needles, which may be recrystallised from hot alcohol, but are decomposed by long boiling, with evolution of nitrogen and formation of salicylic acid. It dissolves in moderately concentrated hydrochloric, hydrobromic, or nitric acid, the solutions on cooling depositing crystalline compounds of these acids with diazosalicylic acid; heated with hydriodic acid, it is converted, with rapid evolution of nitrogen, into iodosalicylic acid. The *hydrochloride*, $C^7H^4N^2O^3.HCl + H^2O$, crystallises in long prisms which are decomposed by water, leaving diazosalicylic acid. Platinic chloride added to the solution of the hydrochloride throws down the platinum salt, $2(C^7H^4N^2O^3.HCl).PtCl^4$, which is likewise decomposed by water, and when heated to about 200°, it yields a sublimate of *monochlorosalicylic acid*, $C^7H^5ClO^3$, in long needles resembling benzoic acid (Schmitt).

Oxysalicylic Acid. $C^7H^6O^4$.—This acid, prepared by Lautemann's process (iv. 320), dissolves in 58·7 pts. of water at 21°, much more freely in hot water; melts at 183° (193° according to Lautemann); reduces ammoniacal silver solution even in the cold; precipitates cuprous oxide from Fehling's solution when heated; and forms with ferric chloride a blue liquid turned blood-red by ammonia (Liechti, *Zeitschr. f. Chem.* [2] vi. 197).

Ethyl oxysalicylate, $C^7H^5O^4.C^2H^5$, obtained by passing hydrochloric acid gas into an alcoholic solution of the acid, and purified by recrystallisation from boiling carbon bisulphide, crystallises from the latter in tufts of colourless, inodorous laminæ. It melts at 78°; cannot be sublimed; dissolves very easily in alcohol and ether; water dissolves a small quantity of it, but very slowly and only after it has deliquesced. It reduces silver nitrate and Fehling's copper-solution; colours ferric chloride dark blue, changing to yellow, and on warming to brown-red; forms with lead acetate a white precipitate soluble in acetic acid. It is decomposed by ammonia, yielding products which have not been accurately investigated (Liechti).

Derivatives of Salicylic Acid containing Alcohol-radicles.

Salicylic acid, having the constitution represented by the formula $C^6H^4\left\{\begin{matrix}OH\\COOH\end{matrix}\right.$, is capable of forming two classes of acid ethers, accordingly as the hydrogen of the hydroxyl or of the carboxyl is replaced by an alcohol-radicle, and neutral ethers in which both these hydrogen-atoms are thus replaced; *e.g.*,

$C^6H^4\left\{\begin{matrix}OC^2H^5\\CO^2H\end{matrix}\right.$	$C^6H^4\left\{\begin{matrix}OH\\CO^2C^2H^5\end{matrix}\right.$	$C^6H^4\left\{\begin{matrix}OC^2H^5\\CO^2CH^3\end{matrix}\right.$
Ethyl-salicylic acid.	Acid ethyl salicylate.	Methylic ethyl-salicylate.

Methyl-salicylic Acid. $C^6H^4\left\{\begin{matrix}OCH^3\\CO^2H\end{matrix}\right.$ (Graebe, *Ann. Ch. Pharm.* cxxxvi. 124; cxxxix. 134).—Obtained by heating 1 pt. of winter-green oil (acid methyl salicylate*) with ½ pt. potassium hydrate (previously dissolved in alcohol) and 1½ to 2 pts. methyl iodide in a closed vessel to 100°–120° for several hours, and decomposing the resulting liquid (decanted from the potassium iodide and freed from excess of methyl iodide) by boiling with caustic soda. On adding hydrochloric acid, methyl-salicylic acid separates, and may be freed from admixed salicylic acid by recrystallisation, or by digestion with milk of lime, whereby calcium salicylate is separated in the insoluble state.

Methyl-salicylic acid crystallises, by slow evaporation of its alcoholic solution, in well-defined prisms, which, according to Rammelsberg's determinations, appear to be monoclinic, exhibiting the combination $\infty P . \infty P \infty . (\infty P \infty) . (P \infty) . 0P$. It dissolves very easily in alcohol and ether, and in about 200 pts. of water at 20°, much more easily in boiling water. The solution has an acid reaction, and is not coloured violet by ferric chloride. The acid melts at 98·5°, under water at 72°. Above 200° it is resolved into anisol (methyl-phenol) and carbon dioxide. Heated with hydriodic acid to 120°–130°, it yields salicylic acid and methyl iodide, and decomposes in a similar manner with hydrochloric acid:

$$C^6H^4\left\{\begin{matrix}OCH^3\\CO^2H\end{matrix}\right. + HI = C^6H^4\left\{\begin{matrix}OH\\CO^2H\end{matrix}\right. + CH^3I.$$

Barium methylsalicylate, $(C^8H^7O^3)^2Ba$, is very soluble, and forms a nodular crystalline mass. The *calcium salt* is slightly soluble in cold water, and crystallises from hot water in large needles. The *lead salt*, $(C^8H^7O^3)^2Pb + H^2O$, forms tufts of sparingly soluble prismatic crystals. The *silver salt*, $C^8H^7O^3Ag$, is a white precipitate, and crystallises from water in stellate groups of needles. The *ethylic ether*, $C^6H^4(OCH^3).CO^2C^2H^5$, formed by Cahour's process (v. 160), or by passing hydrochloric acid gas into an alcoholic solution of the acid, boils at 260° (Graebe).

Methyl-nitrosalicylic acid, $C^6H^3(NO^2)\left\{\begin{matrix}OCH^3\\CO^2H\end{matrix}\right.$, produced by adding methyl-salicylic acid to fuming nitric acid, forms slender colourless needles melting at 149°, solidifying in the crystalline form on cooling, subliming without decomposition, sparingly soluble in cold, easily in boiling water, also in alcohol and ether; does not redden ferric chloride (Kraut).

The acid methyl-ethers of nitro- and dinitro-salicylic acid are formed, with evolution of nitrogen dioxide, by the action of nitrogen tetroxide (nitroso-nitric anhydride) on winter-green oil; *e.g.*,

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* The same methyl-salicylic acid applied to winter-green oil in vol. v. p. 161 is incorrect.

$$\underset{\text{Acid methyl salicylate.}}{C^6H^4\left\{\begin{matrix}OH\\CO^2CH^3\end{matrix}\right.} + \underset{\text{Nitrogen tetroxide.}}{\left.\begin{matrix}NO^2\\NO\end{matrix}\right\}O} = \underset{\text{Nitrous acid.}}{\left.\begin{matrix}H\\NO\end{matrix}\right\}O} + \underset{\text{Acid methyl-nitrosalicylate.}}{C^6H^3(NO^2)\left\{\begin{matrix}OH\\CO^2CH^3\end{matrix}\right.}$$

and

$$3NO^2H = NO^3H + N^2O^2 + H^2O$$

(Bungo, *Zeitschr. f. Chem.* [2] iv. 649).

Ethyl-salicylic Acid. $C^9H^{10}O^3 = C^6H^4\left\{\begin{matrix}OC^2H^5\\CO^2H\end{matrix}\right.$.—The methylic ether of this acid, $C^6H^4(OC^2H^5).CO^2CH^3$, is prepared by heating winter-green oil with equivalent quantities of potassium hydrate and ethyl iodide, or by first converting the winter-green oil into methylic sodium-salicylate, $C^6H^4(ONa).CO^2CH^3$, by treating it with an equivalent quantity of caustic soda mixed with several times its volume of saturated solution of common salt, and heating this sodium compound with ethyl iodide in sealed tubes. When washed with dilute potash, dried, and rectified, it boils at 265°. To obtain ethyl-salicylic acid, the methylic ether is converted into a barium salt by prolonged boiling with baryta-water; this salt, after recrystallisation from alcohol, is decomposed by hydrochloric acid; and the acid thus separated is dissolved out by ether. Ethyl-salicylic acid is a colourless, scentless oil, coagulating at −16° to a viscid nearly solid mass, which, on being removed from the freezing mixture, separates into crystals melting at 19·3 to 19·5°. Its *barium salt*, $(C^9H^9O^3)^2Ba$, is very soluble in water, crystallises from absolute alcohol in interlaced needles, and is precipitated from the alcoholic solution by ether. The *calcium salt*, $(C^9H^9O^3)^2Ca$, crystallises from water in microscopic needles. The *lead salt*, $(C^9H^9O^3)^2Pb + 2H^2O$, forms slender needles, which melt and give off their water at 150°. The *silver salt*, $C^9H^9O^3Ag$, is a white precipitate crystallising from water in tufts of needles (Kraut, Schröder, a. Prinzhorn, *Ann. Ch. Pharm.* cl. 1).

Ethyl-nitrosalicylic acid, $C^9H^9(NO)^2O^3 = C^6H^3(NO^2)\left\{\begin{matrix}OC^2H^5\\CO^2H\end{matrix}\right.$, is obtained by evaporating ethyl-salicylic acid with nitric acid of sp. gr. 1·2 and recrystallising from boiling water, or by heating acid methyl-nitrosalicylate (nitrated winter-green oil) with potash and ethyl iodide, saponifying the resulting methylic ether with potash, and removing unaltered nitrosalicylic acid in the form of basic barium salt. Ethyl-nitrosalicylic acid crystallises from boiling water in colourless silky laminæ; melts at 161; solidifies in the crystalline form on cooling; sublimes without decomposition; does not colour ferric chloride; is nearly insoluble in cold water, but easily soluble in boiling water, also in alcohol and ether. It is isomeric with the acid ethyl-nitrosalicylate, crystallising in yellow needles, prepared by Cahours (v. 166; there called ethyl-nitrosalicylic acid), and probably identical with the acid which Perkin obtained from ethyl-salicylol (p. 1009). The *barium salt*, $[C^9H^8(NO^2)O^3]^2Ba + 2H^2O$, forms colourless, shining, short prisms, often united in crosses, moderately soluble in cold water. The *silver salt* is a white precipitate crystallising from boiling water in needles (Kraut, Schröder, a. Prinzhorn).

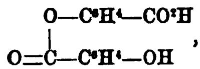
Isopropylsalicylic acid, $C^{10}H^{12}O^3 = C^6H^4\left\{\begin{matrix}OCH(CH^3)^2\\COOH\end{matrix}\right.$, prepared like the ethyl-compound, is a transparent, colourless oil becoming viscid, but not solid at −20°; neither does it solidify when left for a long time over oil of vitriol. It has a strong acid reaction; mixes with alcohol and ether; is nearly insoluble in cold water, somewhat more soluble in boiling water, the solution becoming milky on cooling; does not colour ferric chloride. The *calcium salt*, $(C^{10}H^{11}O^3)^2Ca + 2H^2O$, forms tufts of slender needles very soluble in hot water. The *barium salt*, $(C^{10}H^{11}O^3)^2Ba + H^2O$, separates as a gum from aqueous solution, in needles from an alcoholic solution covered with a layer of ether. The *silver salt*, $2C^{10}H^{11}O^3Ag + H^2O$, crystallises from boiling water in tufts of needles. The *methylic ether*, $C^{10}H^{11}O^3.CH^3$, obtained by heating winter-green oil with isopropyl iodide and alcoholic potash, is an oil having a faint yellow colour, becoming darker on exposure to light; boils at 250°; sp. gr. 1·062 at 20°; dissolves easily in alcohol and ether; does not colour ferric chloride. Heated with alcoholic ammonia, it is converted into the amide $C^{10}H^{11}O^2.NH^2$, which crystallises in feathery needles, soluble in aqueous ammonia or potash, in alcohol and ether; melts in moderately warm water and dissolves therein (Kraut, Schröder, a. Prinzhorn).

Benzyl-salicylic acid, $C^7H^5(C^7H^7)O^3 = C^6H^4(OC^7H^7).CO^2H$, is formed by heating benzoyl chloride with methyl sodium-salicylate and alcohol in a sealed tube to 100°. The resulting liquid evaporated over the water-bath leaves an oil which distils above 320°; and by boiling this oil with alcoholic potash, dissolving the resulting potassium salt in water, and adding hydrochloric acid, benzyl-salicylic acid is obtained as an oil, which solidifies in the course of 24 hours, and may be recrystallised from alcohol, or better from carbon tetrachloride. It melts at 75°, dissolves easily in alcohol, crystallises therefrom in small transparent plates, and is somewhat soluble in boiling water. Its *ammonium salt* is decomposed by evaporation. The *silver salt*, $C^{14}H^{11}O^{3}Ag$, is a white precipitate, melting at 100°. The *lead* and *mercury salts* are white, the *copper salt* is a pale apple-green precipitate (Perkin, *Chem. Soc. J.* vi. 122).

Derivatives of Salicylic Acid containing Organic Acid Radicles.

Acetyl-salicylic acid, $C^{9}H^{8}O^{4} = C^{6}H^{4}\left\{\begin{matrix}OC^{2}H^{3}O\\CO^{2}H\end{matrix}\right.$, first obtained by Gilm (*Ann. Ch. Pharm.* cxii. 180), by the action of acetyl chloride on salicylic acid, is likewise formed by the action of acetyl chloride on sodium salicylate, in which case Gerhardt supposed acetosalicylic anhydride to be formed (*ibid.* lxxxviii. 162); it may be extracted from the product by ether, and remains, after the distillation of the latter, as a nearly colourless oil which quickly crystallises. It separates from boiling water in very loosely aggregated slender needles; has a strong acid reaction; melts when heated, and resolidifies in the crystalline form if it has not been heated above its melting point; the recently fused acid solidifies at 118°–118·5°. It dissolves very sparingly in cold water; melts when heated under water, and is not perceptibly decomposed by prolonged boiling with water; dissolves easily in alcohol, ether, and benzol; colours ferric chloride like salicylic acid; decomposes carbonates; is precipitated by acids without alteration. With excess of hot baryta-water it yields salicylate and acetate. When heated with ammonia it forms ammonium salicylate, and probably acetamide, but no salicylamide (salicylamide is not converted into ammonium salt under the conditions just mentioned) (Kraut, Schröder, a. Prinzhorn).

Salicylosalicylic or **Disalicylic acid,** $C^{14}H^{10}O^{5} = \left.\begin{matrix}(C^{7}H^{4}O)''\\(C^{7}H^{4}O)''\\H^{2}\end{matrix}\right\}O^{3}$ or



$$\begin{array}{l}\text{O}-\text{C}^{6}\text{H}^{4}-\text{CO}^{2}\text{H}\\ \;\;\;|\\ \text{O}=\text{C}-\text{C}^{6}\text{H}^{4}-\text{OH}\end{array}$$

, also called *Salicylic anhydride* (v. 160), is formed when a mixture of acetyl chloride and salicylic acid is heated for some time to 130°–140° in a flask with upright condenser, and separates as a yellowish oil on boiling the product with water; also, together with acetic anhydride, by heating acetyl-salicylic acid to 140°–170°. It is obtained pure by boiling the oil with water, dissolving the remainder in ether, decolorising with animal charcoal, dehydrating, and evaporating. It then forms a transparent amorphous light yellow mass, which by standing over oil of vitriol, or warming, becomes hard, brittle, and friable, and dissolves easily in alcohol, ether, and benzol. When treated with alkaline carbonates, it forms easily soluble salts, from which it is precipitated by acids in its original state. It is converted by aqueous ammonia into salicylamide and ammonium salicylate, and when further heated, gives off 1 mol. water, and leaves trisalicylosalicylic acid, $C^{28}H^{18}O^{9}$, according to the equation: $2C^{14}H^{10}O^{5} = H^{2}O + C^{28}H^{18}O^{9}$.

Trisalicylo-salicylic or **Tetrasalicylic acid,** $C^{28}H^{18}O^{9} = \left.\begin{matrix}4(C^{7}H^{4}O)''\\H^{2}\end{matrix}\right\}O^{5}$ or $HO-(C^{6}H^{4})''-(COOC^{6}H^{4})''-(COOC^{6}H^{4})''-(COOC^{6}H^{4})''-COOH$.—This compound, obtained, as just mentioned, by dehydration of disalicylic acid, is also formed when acetosalicylic acid is heated as long as acetic anhydride continues to go off, and till the temperature has risen to 230°–240°, and a drop of the distillate becomes turbid when mixed with a little water. The viscid residue may then be purified in the same manner as the preceding compound. Tetrasalicylic acid is a thick light yellow oil, which becomes hard and brittle much more quickly than disalicylic acid; softens at about 70°; reacts with solvents, caustic potash, alkaline carbonates, and ammonia, like disalicylic acid; and when further heated, yields salicylic acid, phenol, carbon dioxide, and a body, $C^{6}H^{4}O$, formerly obtained by Limpricht and by Märcker from salicylide (v. 161).

Heptasalicylo-salicylic or **Octosalicylic Acid.** $C^{56}H^{34}O^{17} = \left.\begin{matrix}(C^{7}H^{4}O)^{8}\\H^{2}\end{matrix}\right\}O^{9}$ or $HO-(C^{6}H^{4})''-(CO\overset{''}{O}C^{6}H^{4})^{7}-COOH$.—Prepared by heating 1 pt. phosphorus

oxychloride with 2 or 3 pts. of finely pulverised sodium salicylate to 150° in a flask with upright condenser, till the whole is converted into a viscid mass; expelling the excess of oxychloride in a stream of dry air at 110°; boiling with dilute solution of sodium carbonate, then with water; digesting the dried residue with ether to remove a small quantity of disalicylic acid; again drying the residue, and dissolving it in boiling benzol; pouring the concentrated solution into a large quantity of absolute alcohol; immediately collecting the amorphous flocks which separate on a filter; and freeing them from benzol and alcohol by leaving them over oil of vitriol frequently renewed. Octosalicylic acid thus prepared is a loose white powder, becoming strongly electrical by friction; insoluble in water, ether, and cold alcohol, somewhat soluble in boiling alcohol, easily in benzol; solidifying after fusion to a brittle resin. Heated for three hours to 200°–220° in a stream of hydrogen, it loses 7·2 p. c. of its weight, yielding carbon monoxide, and a sublimate consisting of salicylic acid and the body C^6H^4O, but no water, and leaving unaltered octosalicylic acid. The formation of octosalicylic acid is represented by the equation $8C^7H^6O^3 - 7H^2O = C^{56}H^{34}O^{17}$; it is probably identical with salicylide (v. 161) (Kraut, Schröder, a. Prinzhorn).

SALICYLOL. $C^7H^6O^2 = C^6H^4\begin{cases}OH\\CHO\end{cases}$. *Salicyl Hydride. Salicylic Aldehyd.*—This compound is obtained, according to E. W. Davy (*Laboratory*, p. 361), by distilling poplar-twigs which have lain for some time exposed to the air.

Salicylol is converted by *phosphorus pentabromide* at ordinary temperatures into monobromosalicylol, $C^7H^5BrO^2$, which crystallises in tufts of dentated scales or laminæ melting at 98°–99°. *Pentachloride of phosphorus* acts differently, producing dichlorocresol, $C^7H^6Cl^2O$ (L. Henry, *Zeitschr. f. Chem.* [2] v. 371, 478).

Salicylol unites directly with *acetic anhydride*. A mixture of the two heated for four or five hours to 150° becomes perfectly fluid, but when treated with dilute potash, solidifies to a crystalline mass of the compound $C^7H^6O^2.C^4H^6O^3$. This compound crystallises from alcohol in thick transparent plates with bevelled edges; melts at 103°–104°; distils with partial decomposition; is insoluble in water, sparingly soluble in cold, easily in boiling alcohol; and when heated with water to 150°, is resolved into acetic acid and salicylol. Cold potash does not act upon it. The solution in nitric acid deposits salicylol in the form of an oil, on addition of water. *Methyl-*, *ethyl-*, and *acetyl-salicylol* also unite directly with acetic anhydride, forming crystalline compounds (Perkin, *Chem. Soc. J.* [2] v. 586).

Salicylol is an alcoholic aldehyde, as indicated by the formula above given, and its alcoholic hydrogen may be replaced by alkali-metals, alcohol-radicles, and organic acid radicles.

Sodium-salicylol. $C^6H^4(ONa).CHO$, originally obtained by the action of sodium on salicylol in aqueous solution (v. 169), is more conveniently prepared by treating salicylol with sodium ethylate. Sodium is dissolved in 20 to 30 times its weight of absolute alcohol, and the hot solution is mixed with an equivalent quantity of salicylol, whereupon sodium salicylol immediately begins to separate in golden-yellow laminæ, which may be purified by washing with a little alcohol (Perkin, *Chem. News*, xviii. 110).

Cupric salicylol is decomposed by cyanogen chloride in aqueous solution, yielding salicylol, cupric chloride, and cyanic acid, which is immediately transformed into ammonium carbonate:

$$(C^7H^5O^2)^2Cu + 2CyCl + 2H^2O = 2C^7H^6O^2 + CuCl^2 + 2CyHO.$$

But when gaseous cyanogen chloride is passed over cupric salicylide heated to 100°–120°, cupric cyanide is formed, together with an oil which solidifies on cooling to a mass of silky needles, consisting of chlorosalicylol, $(C^7H^5O^2)^2Cu + 2CyCl = CuCy^2 + 2C^7H^5ClO^2$ (Schiff, *Ann. Ch. Pharm.* cl. 199).

Alcoholic Derivatives of Salicylol.

Methyl-salicylol, $C^6H^4(OCH^3).CHO$, isomeric with anisaldehyde, is formed by heating pulverised sodium-salicylol for two or three hours with rather more than an equal weight of methyl iodide and 2 or 3 mol. alcohol to 135°–140°, and separates on mixing the contents of the tube with water, as a nearly colourless oil, which, after washing with weak potash-solution, distils at 238°. It has a faint odour; is heavier than water, nearly insoluble therein; does not solidify in a freezing mixture; gives off hydrogen when treated with sodium; forms crystallisable, easily soluble compounds with the acid sulphites of alkali-metal. Treated with *bromine* in excess, it is converted into methyl-bromosalicylol, $C^6H^3Br(OCH^3).CHO$, a white solid mass, which crystallises from hot alcohol in flat prisms melting at 113°–114·5°. A mixture of methyl-salicylol and alcoholic *ammonia* becomes syrupy in 24 hours, and yields on evaporation a viscid product perhaps analogous to hydrobenzamide, which is converted at 160°–170° into a base. The solution of methyl-salicylol in *nitric acid* of sp. gr. 1.4 separates, on addition of water, a dark-coloured heavy oil, which by further treatment with nitric acid is converted into a solid nitro-acid (Perkin, *Chem. Soc. J.* [2] v. 418).

Ethyl-salicylol, $C^9H^{10}O^2 = C^6H^4(OC^2H^5).CHO$, prepared like the methyl-compound, is a nearly colourless, heavy, strongly refracting oil, having a faint odour, boiling at 247°–249°, not solidifying at low temperatures, nearly insoluble in water, miscible in all proportions with alcohol and ether; it does not unite with alkalis, but forms crystalline compounds with alkaline bisulphites. The *sodium salt*, $C^9H^{10}O^2.SO^3HNa$, crystallises from warm alcohol in silky needles, from water in long efflorescent prisms, is decomposed by heating to 100°, also by hydrochloric acid and by potash. With *bromine* ethyl-salicylol forms ethyl-bromosalicylol, $C^6H^3Br(OC^2H^5).COH$, which crystallises from alcohol in flat oblique prisms, melts at 67°–68°, and forms a crystalline compound with acid sodium sulphite (Perkin, *loc. cit.*).

A solution of ethyl-salicylol in alcoholic *ammonia* gradually deposits a viscid oil which crystallises on standing and consists of hydro-ethylsalicylamide, $C^{27}H^{30}N^2O^3$, formed according to the equation:

$$3C^9H^{10}O^2 + 2NH^3 = 3H^2O + C^{27}H^{30}N^2O^3.$$

This compound dissolves sparingly in cold, more easily in hot alcohol, and crystallises therefrom, with partial decomposition, in small oblique prisms; melts at 100°; solidifies to a resinous mass; dissolves in hydrochloric acid, not in cold potash-ley; and is converted at 160°–165° into an amorphous isomeric base, ethyl-salidine. This base is very bitter, and forms a platinochloride, $2(C^{27}H^{30}N^2O^3.HCl).PtCl^4$, which is deposited from its alcoholic solution on evaporation as a pale orange-yellow crystalline powder (Perkin).

Fuming nitric acid converts ethyl-salicylol into a dark yellow oil precipitable by water—probably ethyl-nitrosalicylol—which by further treatment with nitric acid is converted into ethyl-nitrosalicylic acid, $C^7H^4(C^2H^5)(NO^2)O^3$. This acid crystallises from alcohol in large pale yellow prisms, melts at 163°, and has a strong acid reaction. Its silver salt is a pale yellow precipitate.

Allyl iodide heated to 160° with sodium-salicylol and alcohol, forms an oily product. With *amyl iodide* an oil is likewise obtained, which forms a crystallisable compound with sodium bisulphite (Perkin).

Benzyl-salicylol, $C^{14}H^{12}O^2 = C^6H^4(OC^7H^7).CHO$, isomeric with benzoïn, is produced by heating a mixture of equivalent quantities of sodium-salicylol and benzyl chloride with several times its volume of alcohol to 120°–140°; filtering from sodium chloride; evaporating; distilling the remaining oily liquid, the greater part of which passes over above 32°; washing the oily distillate with potash-solution, and then agitating it with a strong solution of sodium bisulphite, with which it slowly forms a crystalline compound. These crystals are dissolved in cold water; the solution freed from oily impurities by ether is mixed with sodium carbonate; and the body thereby separated is dissolved in ether, and obtained by evaporation as a viscid oil, which gradually solidifies on agitation, and may be purified by recrystallisation from alcohol. Benzyl-salicylol thus obtained melts at 46°, and boils at a temperature above the range of the mercurial thermometer. When cold it has a faint aromatic odour, like that of cloves; when heated it emits a pungent suffocating odour. It is soluble in ether, carbon-tetrachloride, benzol, and alcohol, from which it crystallises in transparent flat oblique rhombic prisms. It dissolves sparingly in boiling water, and with yellow colour in sulphuric acid and alcoholic potash-solution. It is attacked by bromine and nitric acid, unites with alkaline bisulphites, and forms an oily product when heated with acetic anhydride (Perkin, *Chem. Soc. J.* [2] vi. 122).

Acetyl-salicylol. $C^9H^8O^3$* $= C^6H^4\left\{\begin{matrix}OC^2H^3O\\CHO\end{matrix}\right.$ (Perkin, *Chem. Soc. J.* [2] vi. 53, 181).—This compound, isomeric with coumaric acid, is produced by adding acetic anhydride to pulverised sodium-salicylol suspended in dry ether, decanting the ethereal solution after 24 hours from the sodium acetate produced, and evaporating it over the water-bath. Acetosalicylol then remains in the form of an oil which soon solidifies to a crystalline mass; its formation is represented by the equation:

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* A body having this composition was described by Cahours as obtained by the action of acetyl chloride on salicylol (v. 170). Schüler however did not succeed in preparing it in this way (*Jahresb.* 1857, p. 317); and Perkin (*ibid.* 1867, p. 433) obtained thereby, not acetyl-salicylol, but di-salicylol or parasalicyl (p. 1011). Moreover, the compound obtained by Cahours does not agree in its properties with that produced by the action of acetic anhydride on salicylol.

$$C^6H^4\left\{\begin{matrix}ONa\\COH\end{matrix}\right. + (C^2H^3O)^2O = C^2H^3O(ONa) + C^6H^4\left\{\begin{matrix}OC^2H^3O\\COH\end{matrix}\right. .$$

Acetyl-salicylol melts at 37°, and resolidifies to a satiny crystalline mass; boils at about 253°, and distils with slight decomposition. It dissolves easily in ether and in alcohol, and crystallises therefrom in silky needles; the solutions do not colour ferric chloride purple. By *potash* it is resolved into potassium acetate and potassium salicylol:

$$C^6H^4\left\{\begin{matrix}OC^2H^3O\\COH\end{matrix}\right. + 2HOK = C^2H^3O(OK) + C^6H^4\left\{\begin{matrix}OK\\COH\end{matrix}\right. + H^2O,$$

whereas coumaric acid similarly treated yields acetate and salicylate of potassium, with evolution of hydrogen:

$$C^6H^4\left\{\begin{matrix}C^2H^3O\\COOH\end{matrix}\right. + 2HOK = C^2H^3O(OK) + C^6H^4\left\{\begin{matrix}OH\\CO^2K\end{matrix}\right. + H^2.$$

Acetyl-salicylol is decomposed by boiling with *water*. It unites with *acetic anhydride* when the two are heated together to 150°, forming a crystalline compound, $C^9H^8O^3.C^4H^6O^3$, analogous to that of salicylol (p. 1000). This compound melts at 100°–101°, decomposes when distilled, and separates from solution in acetic anhydride in oblique four-sided tables. It is soluble in ether, carbon tetrachloride, and benzol, easily soluble in hot, sparingly in cold alcohol. By water at 150° it is completely resolved into acetic acid and salicylol.

If instead of adding acetic anhydride to sodium salicylol suspended in ether, and decanting from the sodium acetate as above described, the sodium salicylol be dissolved in acetic anhydride, the solution boiled for a few minutes, and then poured into water, an oily body separates, while sodium acetate remains in solution. On distilling this oil, acetic anhydride passes over first, then salicylol, and finally at 290° coumarin, $C^9H^6O^2$, which crystallises in the receiver. This compound results from dehydration of acetyl-salicylol formed in the first instance: $C^9H^8O^3 - H^2O = C^9H^6O^2$; and its formation appears to depend upon the presence of sodium acetate, inasmuch as acetic anhydride alone produces only acetyl-salicylol. Perhaps the anhydro-acetate, $C^2H^3O^2Na.C^4H^6O^3$ (which Perkin has obtained in needle-shaped crystals by dissolving sodium acetate in acetic anhydride), plays some unexplained part in this reaction.

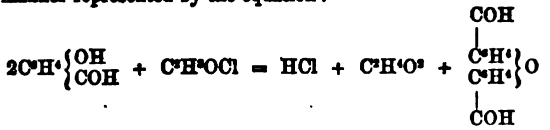
Butyric coumarin, $C^{11}H^{10}O^2$, and *valeric coumarin*, $C^{12}H^{12}O^2$, are obtained in like manner by the action of butyric and valeric anhydrides on sodium-salicylol (p. 500).

Butyryl-salicylol. $C^{11}H^{12}O^3 = C^6H^4\left\{\begin{matrix}OC^4H^7O\\COH\end{matrix}\right.$ (Perkin, *Chem. Soc. J.* [2] vi. 472).—Prepared by leaving an ethereal solution of butyric anhydride in contact with sodium-salicylol for two or three days, then decanting from the sodium-butyrate, and proceeding as in the preparation of the preceding compound. It distils between 260° and 270°, as an oil smelling like butyric acid and salicylol. It is quickly decomposed by strong *potash-solution*, yielding potassium butyrate and potassium salicylol. On heating it to 140°–150° with *acetic anhydride*, and leaving the slightly brown mass in contact with water for two days, crystals are obtained having the composition $C^{13}H^{14}O^6$, and identical with the above-described compound of acetosalicylol with acetic anhydride; an interchange of the radicles acetyl and butyryl must therefore have taken place.

When a mixture of butyrosalicylol, butyric anhydride, and sodium butyrate is heated to boiling for a short time in an open vessel, then washed with water and distilled, the last third of the distillate solidifies on cooling, and when recrystallised from alcohol, yields pure butyric coumarin, $C^{11}H^{10}O^2 = C^{11}H^{12}O^3 - H^2O$; and this compound boiled with potash is converted into butyro-coumaric acid, $C^6H^4\left\{\begin{matrix}C^4H^7O\\COOH\end{matrix}\right.$, isomeric with butyrosalicylol. (See COUMARIN and COUMARIC ACID, pp. 500, 501.)

Benzoyl-salicylol. $C^{14}H^{10}O^3 = C^6H^4\left\{\begin{matrix}OC^7H^5O\\COH\end{matrix}\right.$ (Perkin, *Laboratory*, i. 51; *Zeitschr. f. Chem.* 1867, p. 346).—Produced by the action of benzoyl chloride on sodium-salicylol, and separates on treating the product with water, as a thick oil, which distils at a temperature above the range of the mercurial thermometer. It forms a white pulverulent compound with acid sodium sulphite, and crystalline compounds with the acid sulphites of potassium and sodium. Heated with alcoholic potash it yields benzoic acid and salicylol; with alcoholic ammonia it forms a brown viscid product, together with a crystalline body.

When salicylol is mixed with an equal weight of acetyl chloride, a large quantity of hydrochloric acid is evolved, and the liquid on cooling deposits hard prisms, which when purified by recrysallisation have the composition $C^{14}H^{10}O^3$. The compound thus formed is therefore isomeric with benzoyl-salicylol; it is identical with Ettling's parasalicyl (v. 170), and is regarded by Perkin as disalicylol, its formation taking place in the manner represented by the equation:



$$2C^6H^4\left\{\begin{matrix}OH\\COH\end{matrix}\right. + C^2H^3OCl = HCl + C^2H^4O^2 + \begin{matrix}COH\\|\\\left.\begin{matrix}C^6H^4\\C^6H^4\end{matrix}\right\}O\\|\\COH\end{matrix}$$

Salicylol. Acetyl chloride. Acetic acid. Disalicylol.

The same body is formed by the action of benzoyl chloride (v. 170) and of succinyl chloride on salicylol. It does not unite with alkaline bisulphites, and when heated to 150° with acetyl chloride, is converted into a non-distillable oil, which appears to contain chlorine and acetyl, and is decomposed by boiling potash-ley, with formation of salicylol.

SALICYLOL, AMIDES and UREIDES OF (Schiff, *Zeitschr. f. Chem.* [2] iv, 636; *Ann. Ch. Pharm.* cl. 193).—Salicylol and ethyl-salicylol are acted upon by organic bases at ordinary temperatures, with rise of temperature and elimination of water.

Aniline forms the two compounds:

$$C^6H^4\left\{\begin{matrix}OH\\CH{=}N.C^6H^5\end{matrix}\right. \qquad C^6H^4\left\{\begin{matrix}OC^2H^5\\CH{=}NC^6H^5\end{matrix}\right.$$

Salhydranilide. Ethylsalhydranilide.

Amylamine forms two corresponding hydramylamides. With *ethylaniline* the two following anilides are obtained:

$$C^6H^4\left\{\begin{matrix}OH\\CH(N.C^2H^5.C^6H^5)^2\end{matrix}\right. \qquad C^6H^4\left\{\begin{matrix}OC^2H^5\\CH(N.C^2H^5.C^6H^5)^2\end{matrix}\right.$$

Salhydrethylanilide. Ethyl-salhydrethanilide.

All these anilides are yellow liquids, of aromatic odour, insoluble in water, soluble in alcohol and ether, and destitute of basic properties; they do not form platinochlorides. When exposed to the air, they quickly turn brown, and after a while, especially the ethylic derivatives, assume a deep emerald-green colour.

In cupric salicylol, $(C^7H^5O^2)^2Cu$, the copper replaces the alcoholic hydrogen, the compound retaining its aldehydic properties. Aniline, amylamine, and fused toluidine act upon this compound, with elimination of water; and the product, after washing with water and alcohol, leaves a green shining crystalline mass, which, in the case of aniline and of amylamine, exhibits the composition represented by the following formulæ:

$$\begin{matrix}C^6H^4\left\{\begin{matrix}CH{=}NC^6H^5\\O\end{matrix}\right.\\C^6H^4\left\{\begin{matrix}O\\CH{=}NC^6H^5\end{matrix}\right.\end{matrix}\!\!\left.\begin{matrix}\\\\\end{matrix}\right\}Cu \qquad \begin{matrix}C^6H^4\left\{\begin{matrix}CH{=}NC^5H^{11}\\O\end{matrix}\right.\\C^6H^4\left\{\begin{matrix}O\\CH{=}NC^5H^{11}\end{matrix}\right.\end{matrix}\!\!\left.\begin{matrix}\\\\\end{matrix}\right\}Cu$$

Cupric Salhydranilide. Cupric Salhydramylide.

Ethyl-aniline does not act on cupric salicylol. Toluylene-diamine on the other hand acts upon it at 100°, forming a compound which may be represented as

$$\text{Cupric Salhydrotoluylenamide, } Cu\left\{\begin{matrix}O.C^6H^4.CH{=}N\\O.C^6H^4.CH{=}N\end{matrix}\right\}C^7H^6.$$

When salicylol acts upon urea, either in aqueous solution or in the fused state, the first or second of the following salicyl-ureides is produced:

$$\left.\begin{matrix}CO.N^2H^3\\CO.N^2H^3\end{matrix}\right\}HC.C^6H^4.OH \qquad \begin{matrix}\left.\begin{matrix}CO.N^2H^3\\CO.N^2H^3\end{matrix}\right\}HC.C^6H^4.OH\\\left.CO.N^2H^3\right\}HC.C^6H^4.OH\end{matrix}$$

Diureide. Triureide.

The diureide forms colourless prisms containing 1 mol. water, which is given off in a vacuum. The triureide is a yellow crystalline powder resembling hydrosalicylamide, This latter body is formed, together with cyanuric acid, when the salicyl ureides are heated above their boiling points. The solutions of these ureides form with cupric acetate, olive-green crystalline precipitates consisting of:

Acid Phosphites.—A solution of the normal barium salt in the requisite quantity of phosphorous acid yields, by spontaneous evaporation, radiate groups of white silky needles of the salt $Ba^2H^2P^2O^6 . 3H^3PO^3 + 2H^2O$. A solution of 1 mol. of the normal salt in rather more than 2 mol. phosphorous acid, yields crystals, not of the biacid, but of the *sesqui-acid salt*, $Ba^2H^2P^2O^6 . H^3PO^3 + 8H^2O$, which melts when heated and gives off hydrogen phosphide at 250°. The *biacid salt* crystallises from the solution of the two preceding salts by evaporation over sulphuric acid, with an amount of water corresponding to the formula $BaH^4P^2O^6 + 2H^2O$; ammonia added to the aqueous solution of this salt throws down, not an acid salt as supposed by Rose, but the normal salt. *Zinc Salts.*—By dissolving the neutral zinc salt in phosphorous acid, Rammelsberg obtained various crystallised compounds corresponding to the formulæ $Zn^2H^5P^3O^9 + H^2O$, $Zn^3H^9P^5O^{15} + H^2O$, and $Zn^2H^{11}P^5O^{15}$. An *acid uranic phosphite*, $(\dot{U}O)^3H^3P^2O^6 + 6H^2O$, is obtained, by adding recently precipitated ammonium uranate to the aqueous solution of phosphorus trichloride, as a gradually formed yellow precipitate, which on exposure to the air dries up to hard translucent lumps.

Phosphorous Ethers.—Rammelsberg represents these ethers by formulæ analogous to those of the acid metallic phosphites as follows;

$$\left\{\begin{matrix} H^4P^2O^5 \\ H^2O \end{matrix}\right.$$
Phosphorous acid.

$$\left\{\begin{matrix} H^2BaP^2O^5 \\ H^2O \end{matrix}\right.$$
Acid barium phosphite.

$$\left\{\begin{matrix} (C^2H^5)^4P^2O^5 \\ H^2O \end{matrix}\right.$$
Ethylic phosphite.

$$\left\{\begin{matrix} H^2(C^2H^5)^2P^2O^5 \\ H^2O \end{matrix}\right.$$
Ethylphosphorous acid.

$$\left\{\begin{matrix} (C^2H^5)^4P^2O^5 \\ (C^2H^5)^2O \end{matrix}\right.$$
Triethylic phosphite.

$$\left\{\begin{matrix} Ba(C^2H^5)^2P^2O^5 \\ H^2O \end{matrix}\right.$$
Barium ethylphosphite.

Phosphoric Anhydride, Acid, and **Salts.** On the preparation of phosphoric anhydride on the large scale, see Grabowski (*Ann. Ch. Pharm.* cxxxvi. 119; *Jahresb.* 1865, p. 135).

Mich. Pettenkofer (*Ann. Ch. Pharm.* cxxxviii. 57; *Jahresb.* 1866, p. 138) describes a method of preparing phosphoric acid, simultaneously with hydriodic acid, by treating ordinary phosphorus with iodine and water, distilling off the hydriodic acid, and oxidising the residue, which contains phosphorous and phosphoric acids, with nitric acid.

According to Krämer (*Zeitschr. f. Chem.* [2] v. 543), phosphoric acid may be obtained in transparent prismatic crystals, by evaporating from an aqueous solution, the strength of which is known from its specific gravity, such a quantity of water that the residual liquid shall have exactly the composition H^3PO^4; the acid then crystallises on cooling.

In the purest so-called glacial phosphoric acid of commerce, Brescius (*Zeitschr. anal. Chem.* vi. 187) found 15·3 p. c. soda. He finds that really pure phosphoric acid forms only a soft glutinous mass.

The following table of the relations between the specific gravity and strength of aqueous phosphoric acid (prepared by oxidising amorphous phosphorus with nitric acid) is given by J. Watts (*Chem. News*, xii. 160):

Spec. Grav.	p. c. P^2O^5	Spec. Grav.	p. c. P^2O^5	Spec. Grav.	p. c. P^2O^5	Spec. Grav.	p. c. P^2O^5
1·508	49·60	1·369	39·21	1·236	27·30	1·095	12·18
1·492	48·41	1·356	38·00	1·226	26·36	1·081	10·44
1·476	47·10	1·347	37·37	1·211	24·79	1·073	9·53
1·464	45·63	1·339	36·74	1·197	23·23	1·066	8·62
1·453	45·38	1·328	36·15	1·185	22·07	1·056	7·39
1·442	44·13	1·315	34·82	1·173	20·91	1·047	6·17
1·434	43·95	1·302	33·49	1·162	19·73	1·031	4·15
1·426	43·28	1·293	32·71	1·153	18·81	1·022	3·03
1·418	42·61	1·285	31·94	1·144	17·89	1·014	1·91
1·401	41·60	1·276	31·03	1·136	16·95	1·006	0·790
1·392	40·86	1·268	30·13	1·124	15·64		
1·384	40·12	1·257	29·16	1·113	14·33		
1·376	39·66	1·247	28·24	1·109	13·25		

2·77 lead, 7·19 tin, 2·38 iron, 7·19 antimony, 14·75 arsenic, and 25·12 sulphur (Breithaupt, *Jahresb.* 1866, p. 918).

SANGUINARINE. This alkaloïd, to which J. Schiel assigned the formula $C^{19}H^{17}NO^4$, has been re-examined by Naschold (*J. pr. Chem.* cvi. 385; *Zeitschr. f. Chem.* [2] vi. 119). Prepared from the root of *Sanguinaria canadensis*, it gave by analysis numbers agreeing with the formula $C^{17}H^{15}NO^4$. The *hydrochloride* prepared by saturating the ethereal solution with dry hydrogen chloride has, after drying in a vacuum, the composition $C^{17}H^{15}NO^4.HCl + H^2O$. The *platinochloride* dried at 100° is $2(C^{17}H^{15}NO^4.HCl).PtCl^4$; the *platinocyanide* precipitated by adding a hot solution of potassium platinocyanide to a solution of the sulphate contains $2(C^{17}H^{15}NO^4.HCy).PtCy^4$. Double *gold* and *mercury salts* of complex constitution were also obtained.

SAPONIN and **SAPOGENIN.** Rochleder, from a renewed investigation of saponin and its products of decomposition (*Zeitschr. f. Chem.* [2] iii. 632), deduces for saponin the formula $C^{32}H^{54}O^{18}$, and for sapogenin, $C^{14}H^{22}O^2$, whence the complete decomposition of saponin would be represented by the equation.

$$C^{32}H^{54}O^{18} + 2H^2O = C^{14}H^{22}O^2 + 3C^6H^{12}O^6.$$

Sapogenin is soluble in alcohol and in ether, and crystallises from the former by slow evaporation in concentric groups of needles. From solution in dilute aqueous potash it is precipitated by stronger potash-ley, as flocculent *potassium-sapogenin*; the solution in alcoholic potash is precipitated by water only when the potash is in excess. When sapogenin is heated with potassium hydrate till decomposition commences, part of it is resolved into acetic acid, butyric acid, and a soft brown substance, and the undecomposed portion when separated by potash melts at 128°, whereas before the treatment with potash it does not liquefy at that temperature. The decompositions of saponin formerly mentioned (v. 194) may be explained, in accordance with the composition of sapogenin above given, by supposing that the gelatinous substance resembling quinovin is formed simultaneously with 2 molecules of sugar:

$$\underset{\text{Saponin}}{C^{32}H^{54}O^{18}} + H^2O = \underset{\substack{\text{Gelatinous}\\\text{substance}}}{C^{20}H^{32}O^7} + \underset{\text{Sugar}}{2C^6H^{12}O^6};$$

and that the second product, distinguished from sapogenin by its easy solubility in alcohol, is a compound of sapogenin with 1 mol. sugar:

$$2C^{14}H^{22}O^2 + C^6H^{12}O^6 = C^{34}H^{54}O^9 + H^2O.$$

The compound obtained by Frémy from saponin, and designated as *æsculic acid*, is regarded by Rochleder as $C^{26}H^{42}O^{12}$, and its formation is represented by the equation:

$$C^{32}H^{54}O^{18} = C^{26}H^{42}O^{12} + C^6H^{12}O^6.$$

SARCINE. The following method of estimating this substance, together with xanthine, in muscular flesh is given by Neubauer (*Zeitschr. anal. Chem.* vi. 33; *Jahresb.* 1867, p. 880). The aqueous extract of .250 to .500 grms. of finely chopped meat (freed from albumin by heating) is mixed with basic lead acetate, not in excess; the filtrate freed from lead by hydrogen sulphide is evaporated to 5–10 cub. cent.; the creatine in it is determined by a process already described (p. 501); and the mother-liquor, freed from alcohol, diluted to 100–150 c. c., and made strongly alkaline by ammonia, is mixed with an alkaline solution of silver nitrate. The resulting precipitate is washed with ammoniacal water and dissolved in hot nitric acid of sp. gr. 1·1; and the sarcine double salt, $C^5H^4N^4O.AgNO^3$, which separates on cooling, is collected on a filter after six hours, washed with water till the acid reaction is removed, and weighed after drying at 100°. From the acid filtrate the xanthine may be precipitated by supersaturation with ammonia, in the form of the compound $C^5H^2N^4O.Ag^2O$. By this process Neubauer has found in beef 0·016 to 0·027 p. c. sarcine, in ox-spleen 0·015 p. c., and in extract of meat 0·59 p. c.

SARCOSINE. A compound of this base with zinc chloride, having the composition $2C^3H^7NO^2.ZnCl^2$, is obtained as a crystalline precipitate on mixing the alcoholic solutions of pure sarcosine and zinc chloride; it often separates in the first instance as a syrupy precipitate, which gradually becomes crystalline. 1 pt. of this compound dissolves at ordinary temperatures in 2660 pts. absolute alcohol. It dissolves very easily in water, and separates by spontaneous evaporation in compact nodular radio-crystalline masses consisting of microscopic quadratic prisms not containing water of crystallisation (Buliginsky, *Zeitschr. f. Chem.* [2] iv. 287). According to Podkopaew (*ibid.* 731), the aurochlorides of sarcosine and creatinine, which are easily prepared from the zinco-chlorides, crystallise well, and afford the means of separating the two bases when they occur together.

SARRACENINE. An alkaloïd occurring in the root of *Sarracenia purpurea*. It is bitter, soluble in alcohol and ether, and forms a crystallisable sulphate (St. Martin, *Zeitschr. f. Chem.* [2] ii. 442).

SASSAFRAS OIL (Grimaux a. Ruotte, *Ann. Ch. Pharm.* clii. 88; *Zeitschr. f. Chem.* [2] v. 411).—This oil is a mixture of a lævogyrate hydrocarbon and an optically inactive oxygenated body, together with a small quantity of a phenolic substance, which gives it the power of reducing silver solution. This body may be extracted from the oil by potash, and the alkaline solution mixed with hydrochloric acid deposits a few drops of an oil which smells strongly of eugenic acid and colours ferric chloride green.

The hydrocarbon, safrene, has the composition $C^{10}H^{16}$. Vapour-density, obs. 4·71; calc. 4·7. Boiling point 155°–157°. Sp. gr. 0·8345 at 0°. Rotating power $[a] = -17·5°$.

The portion of the crude oil ($\frac{8}{10}$ of the whole) which passes over in the first distillation between 230° and 236° consists of safrol, $C^{10}H^{10}O^2$, which boils between 231° and 233°, but not constantly, because a small portion of it becomes resinised at the high temperature. Safrol is insoluble in water, is not easily dehydrated by calcium chloride, and for complete purification must be distilled in a stream of dry hydrogen. It smells like sassafras oil; has a sp. gr. of 1·1141 at 0°; is optically inactive; remains liquid at −20°; does not unite with acid sulphites of alkali-metal; does not dissolve sodium; does not act on benzoyl chloride even at the boiling temperature of the latter; does not dissolve in alcoholic potash even at 120°, but is converted by that reagent at 180° into a black uncrystallisable resin. With boiling hydriodic acid (at 127°), it forms a thick green iodated oil. It reduces phosphorus pentachloride to trichloride without formation of oxychloride, and is itself converted into a thick tenacious mass, probably *monochlorosafrol*. A similar product is formed on bringing 1 mol. safrol in contact with 1 mol. bromine; but on adding a large excess of bromine, crystalline *pentabromosafrol*, $C^{10}H^5Br^5O^2$, is produced. To prepare this compound, 5 pts. of bromine are added to a solution of 1 pt. safrol in carbon bisulphide. A large quantity of hydrobromic acid is then evolved, and after a few days crystals separate; and by dissolving these in chloroform, washing the solution with potash-ley, and concentrating, pentabromosafrol is obtained in perfectly white rectangular laminæ. It melts at 169°–170°, is but slightly soluble in alcohol and ether even at the boiling heat, dissolves in about 15 pts. of chloroform. Simultaneously with pentabromosafrol there is formed another brominated product melting at 109°.

Nitric acid, even when very dilute, resinises safrol, with formation of oxalic acid. Fuming nitric acid dissolves it, and converts it into a non-crystallisable body, soluble with blood-red colour in alkalis. Safrol is carbonised by heating with zinc chloride, phosphoric anhydride, or sulphuric acid. Melting potash attacks safrol with difficulty, but sassafras oil distilled over melting potash becomes altered in boiling point, the portions which otherwise distil at 230°–234°, afterwards passing over only at 245°–250°, and chiefly at 247°–248°. This distillate has the same percentage composition as safrol.

SCOPARIN. This substance, the yellow colouring matter of *Spartium scoparium* (v. 208), is resolved, like quercetin, by fusion with potassium hydrate, into phloroglucin and protocatechuic acid, perhaps in the manner represented by the equation:

$$\underset{\text{Scoparin.}}{C^{21}H^{22}O^{10}} + O^5 = \underset{\substack{\text{Phloro-}\\\text{glucin.}}}{C^6H^6O^3} + \underset{\substack{\text{Protocatechuic}\\\text{acid.}}}{2C^7H^6O^4} + CO^2 + 2H^2O$$

(Hlasiwetz, *Ann. Ch. Pharm.* cxxxviii. 190).

SELENIUM. *Allotropic Modifications.*—Red crystallised selenium, the monoclinic modification soluble in carbon bisulphide (v. 222), is intermediate in specific gravity between the black and red amorphous varieties, and may be regarded as analogous to monoclinic sulphur. Selenium abstracts chlorine from sulphur chloride, S^2Cl^2, and forms selenium chloride, Se^2Cl^2. If the selenium is in excess, selenium sulphide remains behind on distillation, soluble in carbon bisulphide, and crystallising therefrom in red prisms. Selenium in either of its modifications dissolves very freely in the chloride, Se^2Cl^2, and separates very slowly on cooling. The selenium thus separated, *in the cold*, belongs to the black modification insoluble in carbon bisulphide. It does not, however, form crystals, but a botryoïdal mass consisting of small spherules. Carbon tetrachloride mixed with traces of carbon selenide (p. 1016) dissolves red selenium in small quantity, but not the black variety. Red selenium is slightly soluble in ethyl sulphide, black selenium insoluble. Ethyl selenide, on the other hand, dissolves both modifications in small and apparently equal quantities. Black selenium appears to be analogous to rhombic sulphur; amorphous red selenium to the variety of sulphur insoluble in carbon bisulphide. The varieties of selenium and sulphur thus compared are formed indeed by similar processes; they are converted in like manner into the other modifications by heating and slow or rapid cooling; and lastly, the specific gravities of these two modifications of selenium differ from one another in the same direction as those of the two modifications of sulphur with which they are compared (Rathke, *Ann. Ch. Pharm.* clii. 181; *Zeitschr. f. Chem.* [2] v. 720).

Crystallised selenium precipitated from selenious acid by potassium bisulphide, and then heated for a week in a drying closet, has a specific heat = 0·08404; selenium separated by the action of the air from solution in potash has the same specific heat = 0·08401. Amorphous selenium obtained by melting and dropping into cold water softens between 40° and 50°. Its specific heat between 25° and 38° is 0·0953; at 50° and above, the specific heat rapidly increases, being 0·1104 at 52°, and 0·1147 at 61° (Bettendorff a. Wüllner, *Zeitschr. f. Chem.* [2] iv. 560).

On the heat of combination of selenium and of hydrogen selenide, see Hautefeuille (*Compt. rend.* lxviii. 1554; *Zeitschr.* [2] v. 487).

On the action of selenium on hydriodic acid, see IODINE (p. 739).

For the estimation of selenium in organic compounds, Rathke (*loc. cit.*) heats the compound to 200° for several hours in a sealed tube with potassium dichromate and nitric acid of sp. gr. 1·4; then evaporates to dryness; heats the residue with hydrochloric acid to reduce the chromic acid; again evaporates several times over the water-bath with hydrochloric as nearly as possible to dryness, to convert the potassium nitrate into chloride; and finally precipitates the selenium by sulphurous acid. An inconvenience attending this process is the slowness with which the potassium nitrate is decomposed by hydrochloric acid; this, however, may be obviated by using free chromic acid instead of potassium chromate.

Selenic and Selenious Acids. J. Thomsen (*Deut. chem. Ges. Ber.* ii. 598) prepares pure *selenious acid* by a method depending on the solubility of barium selenite in free selenious acid. Selenium is dissolved in strong nitric acid; the solution is evaporated to dryness; the residue heated till selenious acid begins to sublime, to expel the excess of nitric acid; the residue is dissolved in water; and to the resulting solution, which may contain selenic and sulphuric as well as selenious acids, baryta-water is added till a filtered sample of the liquid no longer gives a permanent precipitate with a few drops of baryta-water. On evaporating the filtrate and subliming the residue, selenious acid is obtained quite free from selenic and sulphuric acids, and much more permanent in the air than the acid prepared in the ordinary way.

To obtain pure *selenic acid*, the selenious acid prepared as above is dissolved in water and precipitated with silver nitrate or saturated with silver carbonate. The resulting silver selenite, which is nearly insoluble in water, is shaken up with bromine and water, bromine being added at first, and afterwards bromine-water, till the liquid exhibits a faint orange colour. The solution filtered from the silver bromide is then evaporated to the desired degree of concentration. The solution of selenic acid thus prepared is quite free from sulphuric and selenious acids.

Ethylselenious Acid.—When barium ethylsulphate is distilled with potassium selenide, a reddish-yellow liquid is obtained, which, when treated with nitric and then with hydrochloric acid, yields only traces of oily selenethyl chloride, but, as principal product, the crystals described by Joy (ii. 544). From the aqueous solution of these crystals, sulphurous acid throws down pure *ethyl biselenide*, $(C^2H^5)^2Se^2$, boiling at 186°. These crystals, when purified from selenethyl chloride by agitating their aqueous solution with ether, evaporating the remaining aqueous solution over sulphuric acid, and recrystallising from dilute hydrochloric acid, have the composition of hydrochloride of ethyl-selenious acid, $C^2H^5SeO^2H.HCl$. The crystalline compound obtained in like manner by Wöhler and Dean (iii. 991), by treating methyl biselenide with nitric and hydrochloric acids, consists of the analogous compound $CH^3SeO^2H.HCl$ (Rathke).

Respecting unsuccessful attempts made by Rathke to prepare tetrethyl selenide and tetrethyl sulphide, see *Ann. Ch. Pharm.* clii. 208; *Zeitschr. f. Chem.* [2] v. 724.

Selenium Sulphide. The precipitate formed on passing hydrogen sulphide into selenious acid dissolves with reddish-yellow colour in carbon bisulphide, and the solution concentrated till it begins to deposit crystals on cooling, yields by spontaneous evaporation small but well-defined rhombic prisms, having the colour of potassium dichromate, and containing 63 86 p. c. selenium and 35 50 sulphur. By passing hydrogen selenide mixed with a large excess of hydrogen, first through water, and then through aqueous sulphurous acid, dissolving the resulting precipitate in carbon bisulphide, and submitting the solution to fractional crystallisation, crystals are obtained having the composition 2Se + S, but consisting, not of the pure compound Se^2S, but of a mixture of that compound with SeS^2 and free selenium. The precipitate obtained by passing hydrogen sulphide through selenious acid has the composition Se + 2S, and consists mainly of SeS^2, but contains also Se^2S, probably mixed, not with a higher sulphide of selenium, but with free sulphur (Rathke).

Carbon Biselenide, CSe^2, is produced in small quantity by the action of moist vapour of carbon tetrachloride on phosphorus selenide, the nascent hydrogen selenide resulting from the action of the aqueous vapour on the phosphorus selenide acting on the carbon chloride, according to the equation $CCl^4 + 2H^2Se = 4HCl + CSe^2$. (See CARBON-COMPOUNDS, p. 408.) When the solution of carbon selenide in carbon tetrachloride thus obtained is mixed with alcoholic potash, it assumes a deep red colour; and on mixing the solution with water, which separates carbon tetrachloride, adding hydrochloric acid, and heating the liquid after some time, a dark solid mass separates from it saturated with an oil. This mass, separated from the watery liquid and distilled in a small bent tube, yields a golden-yellow liquid having an intolerable odour and consisting of *ethylic selenio-xanthate*, $C^5H^{10}Se^2O$. When the liquid containing the carbon selenide is dropped into a concentrated solution of potash in absolute alcohol, *potassium selenio-xanthate*, $C^3H^5Se^2OK$, separates in yellow, very deliquescent needles, the alkaline aqueous solution of which yields selenide of lead when heated with lead acetate. The solution decolorises a solution of iodine in potassium iodide, becoming turbid at the same time (Rathke).

SENNA. According to Dragendorff a. Kubly (*Zeitschr. f. Chem.* [2] ii. 411), the active principle of senna-leaves is a glucoside, which they designate as *cathartic acid* (p. 417).

SERICIN and **SERIN.** See SILK.

SERICOGRAPHIS MOHITLI. An acanthaceous plant used in Mexico as a remedy for dysentery, and containing a blue colouring matter called *mohitlin* (p. 831).

SERPENTINE. For analyses of this mineral from various localities, see *Jahresb. f. Chem.* 1860, 774; 1861, 1004; 1862, p. 745; 1863, p. 856; 1866, p. 931; 1867, pp. 996, 1016, 1026.

SIDEROPLESITE. A carbonate of iron and magnesia occurring near Dienten in Salzburg, in the greywacke formation, in lenticular forms, accompanied by dolomite rhombohedrons and rock crystal. Sp. gr. = 3·699. Angle of terminal edges of the cleavage-rhombohedron = 107° 5′ 16″. Its analysis gave

CO^2	FeO	MnO	MgO	CaO	Fe^2O^3	
40·31	43·86	2·57	10·46	0·40	4·07	= 101·67

Reckoning the ferric oxide as ferrous carbonate, the mineral may be represented by the formula $3CO^3Fe.3CO^3Mg$ (Zepharovich, *Jahresb.* 1866, p. 906).

SILICA. The constitution of silica (whether SiO^2 or SiO^3) has been discussed by Scheerer (*J. pr. Chem.* xci. 415; *Jahresb.* 1864, p. 310); Ordway (*Sill. Am. J.* [2] xl. 187; *Jahresb.* 1866, p. 192); and Geuther (*Jenaische Zeitschr.* iv. 313; *Jahresb.* 1868, p. 206).

Modifications.—An amorphous silica of sp. gr. 2·6, differing from the ordinary variety (sp. gr. 2·2), is formed, according to Jenzsch (*Pogg. Ann.* cxxvi. 467; *Jahresb.* 1865, p. 875), by the weathering of chalcedony. G. vom Rath (*Pogg. Ann.* cxxxiii. 507; cxxxv. 437; *Zeitschr. f. Chem.* [2] iv. 666; v. 410), has discovered in a volcanic porphyry from the Cerro S. Cristobal, near Pachuca in Mexico, a new mineral, which he designates as *tridymite*, consisting of crystallised silica of sp. gr. 2·3, whereas ordinary crystallised silica has the sp. gr. 2·6, and silica of sp. gr. 2·3 has hitherto been observed only in the amorphous state.

On the preparation of crystallised silica in the dry way, see G. Rose (*Zeitschr. f. Chem.* [2] v. 646). On Graham's colloïd silica, see vol. v. pp. 241, 1088.

Hydrates (Merz, *J. pr. Chem.* xcix. 177).—Gelatinous silica obtained by decomposing gaseous silicon fluoride with water, continuously washed, with frequent pressure, dried, pulverised, and again washed, first with ammoniacal and then with pure water, retained, after six weeks' drying in the air at 20°–25°, from 13·1 to 13·5 p. c. water, answering to the formula $2SiO^2.H^2O$; the amount of water was diminished by exposure over sulphuric acid, but was recovered on exposure to the air. After drying at 60°, or after prolonged desiccation over sulphuric acid, the hydrate $3SiO^2.H^2O$ remained (containing 8·68 and 9·24 p. c. water; calc. 9·04 p. c.); at 80°–100° the very unstable hydrate $4SiO^2.H^2O$ (containing 6·17 to 7·40 p. c. water; calc. 6·93 p. c.); after drying at 250°–270°, the amount of water (3·29 to 3·59 p. c.) agreed with the formula $8SiO^2.H^2O$. Recently prepared silica retains smaller quantities of water at the several temperatures above cited (at 70° only about 6 p. c.; at 90°, 4·6 p. c.; at 100°, 4·3 p. c.; at 130°, 3·5 p. c.; at 160°, 3 p. c.); it appears therefore to undergo a gradual molecular alteration.

The hydrates, together with the monohydrate obtained by Graham, form the following series:

$SiO^2.H^2O$ $\qquad$ $4SiO^2.H^2O$
$2SiO^2.H^2O$ $\qquad$ $8SiO^2.H^2O$
$3SiO^2.H^2O$

The third and fourth of these were previously obtained by Fuchs (v. 242). The hydrates $3SiO^2.2H^2O$ and $2SiO^2.3H^2O$, described by Ebelmen and Doveri, do not appear to have been obtained by Merz. The hydrate obtained by the action of moist air on silicon tetrachloride has, according to Langlois (*Jahresb.* 1858, p. 140), the composition $9SiO^2.4H^2O$.

Solubility in Ammonia.—According to Wittstein (*Jahresb.* 1866, p. 192), ammonia dissolves perceptible quantities of amorphous silica, not only in the gelatinous, but also in the dry and ignited state; even pulverised quartz is attacked by it. When a clear solution of water-glass supersaturated with hydrochloric acid is gradually mixed with ammonia, a strong flocculent turbidity is produced, which, however, disappears on addition of more ammonia, either in the cold or at a gentle heat. 100 pts. of aqueous ammonia containing 10 p. c. NH^3 dissolve, of:

Crystallised silica	0·017 pt.
Amorphous silica, ignited	0·38 „
Amorphous silica, as hydrate*	0·21 „
Amorphous silica, in the form of jelly	0·71 „

The solutions prepared by contact of the silica with the aqueous ammonia in closed vessels for several days sometimes clarified but slowly; that obtained with the gelatinous acid was slightly opalescent. By prolonged exposure to the air they lost their alkaline reaction, and then contained 4 eq. silica to 1 eq. ammonia. This neutral solution when boiled and evaporated does not yield any deposit, although $\frac{19}{20}$ of the ammonia has been driven off, and only 1 eq. ammonia remains in the liquid to 80 eq. silica. After complete evaporation there remains an amorphous, laminar, horny, translucent residue, likewise containing 80 eq. silica to 1 eq. ammonia, and nearly insoluble in water.

Solubility in Acids.—Wittstein has likewise observed that hydrated silica, at the moment of separation (as when cast iron or steel is dissolved in an acid), is more abundantly dissolved by nitromuriatic acid (3 pts. hydrochloric acid of sp. gr. 1·13 to 1 pt. nitric acid of sp. gr. 1·33) than by hydrochloric acid (sp. gr. 1·13) (*Jahresb.* 1868, p. 207).

SILICATES. On the classification of silicates, see Wurtz (*Chem. Soc. J.* xv. 397; *Rép. Chim. pure*, ii. 449);—Weltzien (*Systematische Uebersicht der Silicate*, Giessen, 1864; *Jahresb.* 1864, p. 211);—Schiff (*Ann. Ch. Pharm. Suppl.* iv. 27; *Jahresb.* 1865, p. 194);—Frémy (*Compt. rend.* lxiv. 243; *Jahresb.* 1867, p. 202).

Cleve and A. E. Nordenskjöld (*J. pr. Chem.* c. 119; *Jahresb.* 1867, p. 989) designate a number of hydrated hygroscopic silicates, formed on the type of hisingerite, as *ferruginous colloïdal silicates*, and represent them by the following formulæ:

Hisingerite . . .	$(2MO.Fe^2O^3)^2SiO^2 + 4H^2O$.
Scotiolite . . .	$(2MO.Fe^2O^3)^2SiO^2 + 3H^2O$.
Traulite . . .	$3Fe^2O^3.5SiO^2 + 10H^2O$.
Neotokite and Stratopeite	$(MnO; FeO; MgO; PbO)^6.5SiO^2 + 7H^2O + xO$.
Wittingite . . .	$4MnO.5SiO^2 + 9H^2O + xO$.
Gillingite . . .	$(2MO.R^2O^3)^4.5SiO^2 + 9H^2O$.

On the formation of natural silicates, and the alteration of the specific gravity of silicates by heat, see F. Mohr (*Kölnische Zeitung*, 1865, Nr. 156; *Jahrb. Min.* 1866, p. 181; *Jahresb.* 1866, p. 911), and C. W. Fuchs (*Jahrb. Min.* 1865, p. 576; *Jahresb.* 1865, p. 865).

Daubrée (*Compt. rend.* lxiv. 339; *Jahresb.* 1867, p. 1010) has made experiments on the action of water on various silicates under conditions analogous to those which occur in nature. The minerals were enclosed, together with an equal or a double weight of water, in cylindrical vessels of stone-ware or iron, which were made to rotate upon horizontal axes with a velocity equivalent to a rectilinear motion of 2500 metres per second. Felspar thus treated in a stone-ware cylinder with pure water was somewhat easily attacked, giving up to the water, potash, silica, alumina and traces of sulphuric and hydrochloric acids; in the iron vessel, the silica was precipitated by the ferric hydrate formed by the oxidation of abraded iron. Three kilograms of felspar fragments rotated in the iron cylinder for 192 hours (corresponding to a distance of 460 kilometres), yielded 2720 grms. of mud, and the 5 litres of water took up 12·6 grm. potash: consequently from 2 to 3 p. c. of potash present in the dust had passed into solution. Water containing sodium chloride (3 p. c.) and carbonic acid water acted less quickly than pure water. Obsidian and leucitophyre were but very slightly attacked by pure water. With serpentine, obsidian, and angular lumps of felspar, the quantity of abraded powder amounted to 0·3 p. c.; with rounded lumps of felspar, to 0·2 p. c.; with flints, to 0·02 p. c. The state of the solid substance has some influence on its decomposibility; felspar which had been heated to whiteness and rapidly cooled was decomposed with increased facility. The abraded felspar powder exhibited considerable similarity to many clay-slates and lithomarges.

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* Prepared from the hydrochloric acid solution by evaporation, washing, and drying, and containing a quantity of water answering to the formula $3SiO^2.4H^2O$.

On the decomposition of silicates and other crystallised compounds by electro-capillary diffusion, see Becquerel (*Compt. rend.* lxvii. 1081; *Zeitschr. f. Chem.* [2] v. 134).

For the decomposition of silicates in analysis, in cases in which the alkalis are to be determined, R. Hoffmann (*Zeitschr. anal. Chem.* vi. 366) recommends, instead of aqueous hydrofluoric acid, the use of ammonium fluoride with addition of sulphuric acid. The finely pulverised silicate is mixed with 3 or 4 pts. of pure ammonium fluoride, moistened in a platinum dish with sulphuric acid, and heated, with frequent addition of sulphuric acid, first over the water-bath, then over an open flame, till all the acid is expelled. The residue is dissolved in hydrochloric acid; the solution precipitated with ammonia and ammonium carbonate; then—after removing the sulphuric acid by barium chloride in case of magnesia being present—evaporated to dryness with addition of oxalic acid, and ignited. On heating the residue with water, the alkalis pass into solution.

According to F. Mohr (*Zeitschr. f. Chem.* v. 308), the decomposition of silicates by fluorides is greatly facilitated by previously submitting them in the pulverised state to intense ignition. They are then rapidly decomposed by gaseous hydrofluoric acid without formation of the insoluble residue which so often occurs when unignited silicates are treated with hydrofluoric acid.

On the decomposition of silicates by hydrofluoric acid, see Maskelyne (*Chem. News*, xxi. 27; *Zeitschr. f. Chem.* [2] vi. 191).

Sodium metasilicate is obtained in monoclinic crystals containing $Na^2SiO^3 + 8H^2O$, by dissolving ignited silica in an equivalent quantity of caustic soda-ley, evaporating the decanted solution with as little contact of air as possible, till a number of small crystals of sodium carbonate fall down; then cooling the solution to −22°, and stirring it with a glass rod till it solidifies to a crystalline pulp; straining this mass to free it from the mother-liquor; dissolving it in a small quantity of distilled water; and leaving the solution to itself (Ammon, *Jahresb.* 1862, p. 138). According to Ordway (*Sill. Am. J.* [2] xl. 186), the same salt is easily prepared by dissolving the liquid layer obtained by precipitating a purified solution of soda water-glass (1 mol. Na^2O, 2·25 mol. SiO^2) with twice its volume of alcohol, in an equal weight of soda-ley of sp. gr. 1·32, and exposing the solution to a low temperature; the crystals which form in a few hours may be purified by recrystallisation from water. The salt melts at 45° to a syrup which does not resolidify; at a higher temperature it gives off its water, leaving a spongy mass, which is still easily soluble in water (Ammon). It has not been found possible to prepare a crystallised silicate of potassium or a crystallised double silicate of potassium and sodium by either of the processes above mentioned.

The metasilicates of the earth-metals may be prepared by precipitating a dilute solution of the sodium salt with a solution, mostly diluted, of an earth-metal salt. The *barium salt*, $BaSiO^3$ or $BaO.SiO^2$, is not quite insoluble in hot water, perfectly soluble in dilute hydrochloric acid, and retains a somewhat considerable quantity of water even after drying at 100°. The *calcium salt*, $CaSiO^3$ or $CaO.SiO^2$, is a white, very bulky, gelatinous precipitate, which also retains water with great obstinacy, and when left in contact with water for a long time, dissolves in it, apparently with partial decomposition. The *strontium salt* is exactly similar in composition and properties. The *magnesium salt*, $3MgSiO^3 + 5H^2O$, is soluble in dilute acids, is not completely decomposed by hydrochloric acid after ignition, and bakes together when strongly ignited. When recently precipitated alumina is added to a moderately concentrated and boiling solution of caustic soda and sodium silicate, all the alumina dissolves in the first instance, but afterwards a white powder is deposited consisting of a *sodio-aluminic silicate*. The reaction appears to be as follows:

$$2(Na^2O.Al^2O^3) + 4(Na^2O.SiO^2) = (2Na^2O.SiO^2 + 2Al^2O^3.3SiO^2) + 4Na^2O.$$

When a hot dilute solution of alum is precipitated with sodium silicate, a gelatinous precipitate is formed, whitish and very light when dry, consisting of a double silicate in which the oxygen of the silica is double that of the bases—that is to say, of a metasilicate:

$$(K^2O.SO^3 + Al^2O^3.3SO^3) + 4(Na^2O.SiO^2) = K^2O.SO^3 + 3Na^2O.SO^3 + Na^2O.SiO^2 + Al^2O^3.3SiO^2.$$

A similar experiment with excess of aluminium sulphate and sodium silicate also gave a metasilicate of aluminium. Results for the most part similar were obtained with silicate of potassium (Ammon).

Acid calcium silicate, $CaO.3SiO^2 + 2H^2O$ or $CaSiO^3.2SiO^2 + 2H^2O$, is obtained on mixing calcium chloride with acid potassium silicate, $K^2O.3SiO^2$, as a gelatinous precipitate which gradually becomes crystalline under the liquid, and when dried at 100° has the composition above given; it does not harden when mixed, either in the air-dried or in the ignited state, with calcium hydrate, or a solution of that substance in sugar-water. *Acid magnesium silicate*, $MgO.2SiO^2 + 2H^2O$, is obtained in like manner as a gelatinous precipitate which does not become crystalline in contact with the liquid (Heldt, *J. pr. Chem.* xciv. 129, 157).

SILICIC CHLOROFORM. The silicohydric chloride (v. 268) which Wöhler a. Buff obtained in 1857 by passing hydrochloric acid gas over heated crystallised silicon, and to which Wöhler assigned the formula $Si^3H^4Cl^{13} = 3SiCl^3.4HCl$, has been shown by Friedel a. Ladenburg (*Bull. Soc. Chim.* [2] vii. 322) to be a mixture separable by repeated fractional distillation into a portion boiling between 35° and 37°, and another boiling between 55° and 60°. The latter is silicic chloride, $SiCl^4$. The former consists of silicic chloroform, $SiHCl^3$, having a vapour-density = 4·64 (calc. 4·69). This compound possesses all the essential characters of the silicohydric chloride described by Wöhler a. Buff: its vapour mixed with air takes fire even by contact with a hot body. From the tetrachloride, which it resembles in appearance and in odour, it is immediately distinguished by its property of being decomposed by water, with evolution of hydrogen. *Chlorine* decomposes it at ordinary temperatures, forming silicic chloride and hydrochloric acid: $SiHCl^3 + Cl^2 = SiCl^4 + HCl$; *bromine* appears not to act on it below 100°. The white oxide produced in the decomposition of silicic chloroform by water, and regarded by Wöhler a. Buff (v. 274) as $3SiO.2H^2O$, afterwards by Wöhler as more probably consisting either of $Si^8H^{10}O^{10}$ or of $Si^3H^4O^6$, and by Geuther (*Jahresb.* 1865, p. 189) as $2SiO^3.HO$ [$Si = 21$], is prepared by Friedel a. Ladenburg by slowly passing the vapour of pure silicic chloroform through a tube with a funnel-shaped termination into water at 0°, filtering quickly, washing the precipitate with ice-cold water, and drying it first over oil of vitriol, then at 150°. In this state it has the composition of silicic formanhydride, $SiH^2O^3 = (SiOH)^2O$, analogous to the unknown formic anhydride $(COH)^2O$. Its formation is represented by the equation:

$$2SiHCl^3 + 3H^2O = 6HCl + (SiOH)^2O$$

(Friedel a. Ladenburg, *Bull. Soc. Chim.* [2] vii. 322).

SILICIC ETHERS. When chlorine is passed into well-cooled silicon-ethyl (v. 266), the liquid first turns yellow, then suddenly colourless, and gives off hydrochloric acid. If the product be distilled after some time, and the portion boiling below 160° again treated with chlorine, these operations being repeated several times, there is finally obtained a liquid boiling between 180° and 220°, and yielding by fractional distillation a small quantity of the compound $SiC^8H^{19}Cl$, which may be regarded either as *silicic monochlorotetrethyl*, derived from silicon-ethyl, $Si(C^2H^5)^4$, by substitution of 1 at. Cl for H, or as the *chloride of siliconongl*, SiC^8H^{19}, a radicle derived from nonyl, C^9H^{19}, by substitution of 1 at. silicon for carbon. The greater portion of the crude product distils between 190° and 195°, and has the composition of *silicic mono-* and *di-chlorotetrethyl* in equivalent proportions; but on continuing the distillation, the composition of the distillate approaches more nearly to that of the latter, and at 230° decomposition takes place. If the portion of the product which distils between 180° and 200° be heated with potassium acetate and alcohol in sealed tubes to 130°–140°, the dichlorinated compound is alone attacked; and on mixing the contents of the tube with water, and heating the oily liquid which separates with strong sulphuric acid, several ethereal compounds are dissolved—including *triethyl-silicic oxide*, $[Si(C^2H^5)^3]^2O$, formed from the silicic dichlorotetrethyl—while *silicic monochlorotetrethyl*, or *siliconyl chloride*, remains undissolved, and distils for the most part between 180° and 190°. On again heating this distillate to 180° with an alcoholic solution of potassium acetate, and mixing the contents of the tube with water, an oily product is obtained, which may be freed from undecomposed silicononyl chloride by treatment with strong sulphuric acid. The resulting solution poured into water deposits *silicononyl acetate*, $\left.\begin{matrix}SiC^9H^{19}\\C^2H^3O\end{matrix}\right\}O$, as a liquid which boils between 208° and 214°, smells like acetic acid, and burns with a bright flame, giving off acetic acid. This liquid treated at 120°-130° with a solution of potash in aqueous alcohol yields *silicononyl alcohol*, $\left.\begin{matrix}SiC^9H^{19}\\H\end{matrix}\right\}O$, as a liquid insoluble in water, smelling like camphor, and boiling at 190°. Sodium dissolves in this alcohol, with evolution of hydrogen, forming a gelatinous substance which is decomposed by water, reproducing the original alcohol.

Triethylic Silicoformate, $SiH(OC^2H^5)^3$ or $\left.\begin{matrix}(SiH)'''\\(C^2H^5)^3\end{matrix}\right\}O^3$, analogous to the tribasic formic ether discovered by Williamson a. Kay, is produced by dropping absolute alcohol into silicic chloroform contained in a long-necked flask. On gently heating the liquid after the reaction is over, and then distilling, the triethylic silicoformate is obtained, as a colourless, very hygroscopic liquid, boiling at 134°, and smelling like normal silicic ether: its vapour forms an explosive mixture with air. It is slowly attacked by water, quickly and with evolution of hydrogen by ammonia and potash. In contact with sodium it is resolved into tetrethylic silicate and silicic hydride, SiH^4 (p. 1021): $4SiH(OC^2H^5)^3 = 3Si(OC^2H^5)^4 + SiH^4$. The mode of action of the sodium has not been explained; it cannot be replaced by platinum-black (Friedel a. Ladenburg, *Bull. Soc. Chim.* [2] vii. 322).

Triethylic Silicochloroformate or *Ethylsilicic Monochlorhydrin*, $SiCl(OC^2H^5)^3$, discovered by Friedel a. Crafts (v. 264), is easily prepared by dropping 3 mol. absolute alcohol into 1 mol. silicic chloride, $SiCl^4$, fractionating the product, and collecting apart the portion which passes over at about 156°. It is not acted upon by zinc-ethyl even at the boiling heat (Friedel a. Ladenburg).

Triethylic Silicopropionate or *Tribasic Silicopropionic ether*, $SiC^2H^5(OC^2H^5)^3 = \left.\begin{matrix}(SiC^2H^5)'''\\(C^2H^5)^3\end{matrix}\right\}O^3$, is produced by adding a few lumps of sodium to a mixture of 1 mol. zinc-ethyl and 2 mol. silicochloroformate, and applying a gentle heat, whereupon the action begins, and becomes very violent if not moderated, gas being copiously evolved, consisting chiefly of ethyl chloride, followed by ethyl and ethyl hydride (butane and ethane), while the sodium becomes covered with zinc-powder and gradually disappears. On distilling the mixture after the evolution of gas has ceased, and repeatedly fractionating, tribasic silicopropionic ether is obtained as the chief product, boiling between 159° and 162°, having a sp. gr. of 0·9207 at 0°, and vapour-density = 6·92 (calc. 6·65). It may be regarded as tribasic silicoformic ether, in which the hydrogen immediately connected with the silicon is replaced by ethyl, or as the triethylhydrin of a glycerin, in whose trivalent radicle, C^3H^5, 1 at. carbon is replaced by silicon. It is an ethereal liquid of agreeable odour, resembling that of tetrethylic silicate; insoluble in water, miscible in all proportions with alcohol and ether. By moisture it is gradually resolved into alcohol and products boiling at higher temperatures, doubtless polysilicates analogous to those formed from normal silicic ether. It is not completely decomposed by ammonia. Like normal silicic ether, it is very stable, and is not oxidised by nitric acid till heated above 200°. Strong sulphuric acid decomposes it instantly. Heated with very strong potash-ley, it is quickly decomposed, with formation of two layers of liquid, both of which are dissolved by water, with separation of oil-drops. On neutralising the resulting solution with hydrochloric acid, or, better, on adding sal-ammoniac to the neutral liquid, a white flocculent precipitate separates resembling silica. This precipitate dried over sulphuric acid forms a white powder which blackens and burns when heated on platinum-foil. It dissolves in potash and is reprecipitated by hydrochloric acid. The slightly alkaline solution forms with silver nitrate a white or yellowish precipitate containing silver oxide and silicopropionic acid, $C^2H^5.SiO^2H$. Tribasic silicopropionic ether is therefore decomposed by potash in the manner represented by the equation:

$$SiC^2H^5(OC^2H^5)^3 + 2H^2O = 3C^2H^6O + C^2H^5.SiO^2H.$$

the decomposition being analogous to that of tribasic formic ether:

$$CH(OC^2H^5)^3 + 2H^2O = 3C^2H^6O + H.CO^2H.$$

When triethylic silicoformate is treated in presence of sodium with 1 mol. (instead of ½ mol.) zinc-ethyl, the reaction takes place in the manner above described, but the product boils at a lower temperature and contains more carbon. This body, which boils between 155° and 156°, consists of $Si(C^2H^5)^2(OC^2H^5)^2$, and appears to be produced by reduction of tribasic silicopropionic ether at the moment of its formation. The same compound would be formed by the action of zinc-ethyl and sodium on dichlorosilicic ether (Friedel a. Ladenburg (*Compt. rend.* lxvi. 816; *Zeitschr. f. Chem.* [2] iv. 567; *Jahresb.* 1868, 427).

Trichlorosilicic oxide, $O\left\{\begin{matrix}SiCl^3\\SiCl^3\end{matrix}\right.$, analogous to perchloromethylic ether, $(CCl^3)^2O^2$, is formed by passing the vapour of silicic chloride through an exhausted porcelain tube containing fragments of felspar, and heated nearly to the melting point of the latter. By repeating the same treatment several times with the more volatile portion of the condensed product, a considerable quantity of a mixture is at length obtained, which volatilises above 70°, and may be resolved by fractional distillation into silicic chloride and trichlorosilicic oxide, the latter passing over between 136° and 139°. The oxygen is derived from the felspar, as is shown by the corrosion of the fragments and the presence of solidified drops of alkali-metal chlorides. Trichlorosilicic oxide is also formed, together with phosphorus oxychloride, by passing silicic chloride over strongly heated phosphoric anhydride. Trichlorosilicic oxide is a colourless fuming liquid, having a vapour-density = 10·05 (calc. 9·86). It is decomposed by water like the tetrachloride, and is converted by absolute alcohol into disilico-hexethylic ether, $O\left\{\begin{matrix}Si(OC^2H^5)^3\\Si(OC^2H^5)^3\end{matrix}\right.$, which may be separated from the product by fractional distillation, and boils at 235°–237°. When 1 mol. trichlorosilicic oxide is heated to 180° in a sealed tube for 16 to 18 hours with 3 mol. zinc-ethyl, triethyl-silicic oxide is produced:

$$O\left\{\begin{matrix}SiCl^3\\SiCl^3\end{matrix}\right. + 3Zn(C^2H^5)^2 = 3ZnCl^2 + O\left\{\begin{matrix}Si(C^2H^5)^3\\Si(C^2H^5)^3\end{matrix}\right.$$

(Friedel a. Ladenburg, *Bull. Soc. Chim.* [2] ix. 358).

SILICIC HYDRIDE, SiH^4, originally obtained mixed with hydrogen by the action of hydrochloric acid on magnesium silicide (Wöhler a. Buff, v. 273), may be prepared in the pure state by decomposition of triethylic silicoformate (p. 1020) in contact with sodium:

$$\underset{\text{Triethylic Silicoformate.}}{4SiH(OC^2H^5)^3} = \underset{\text{Silicic hydride.}}{SiH^4} + \underset{\text{Tetrethylic silicate.}}{3Si(OC^2H^5)^4}$$

Silicic hydride thus obtained is a colourless gas, agreeing in all essential characters with that described by Wöhler a. Buff, but not spontaneously inflammable at ordinary pressure and temperature, but only when gently heated under reduced pressure, or when diluted with hydrogen. If a hot knife-blade be held near the bubbles of the gas as they rise over mercury, they take fire with explosion, and the mercury becomes sufficiently heated to set fire to the following bubble; in a eudiometer, also, the gas takes fire on admission of air, if the column of mercury is between 100° and 150° mm. high. Pure silicic hydride decomposed by potash yields 4 volumes of hydrogen, according to the equation:

$$SiH^4 + 2KHO + H^2O = SiO^3K^2 + 4H^2$$

(Friedel a. Ladenburg). Silicic hydride (impure prepared from magnesium silicide) is decomposed by *bromine*, forming a solid and a liquid compound, ($SiBr^4$?), the former crystallising in needles. With *iodine* it forms $SiHI^3$ and SiI^4. It is also decomposed by the chlorides of sulphur, phosphorus, antimony, and tin (Mahn, *Zeitschr. f. Chem.* [2] v. 730).

SILICIC IODIDES. The *tetriodide*, SiI^4, is produced by passing iodine-vapour in a stream of carbon dioxide through a long porcelain tube nearly filled with silicon and heated to redness, and sublimes in the cooler part of the tube as a white crystalline mass. If the iodine is in excess, the product is mixed with free iodine, which may be removed by solution in carbon bisulphide (which easily dissolves the silicic iodide), and agitation of the solution with metallic mercury. Silicic iodide, SiI^4, crystallises by sublimation, or by cooling or evaporation of its solution in carbon bisulphide, in colourless transparent regular octohedrons, which do not act upon polarised light; smaller quantities crystallise in dendritic forms. It melts at 120·5° to a yellowish liquid, and resolidifies to a mass having a silky lustre and usually coloured red by separated iodine. It boils at about 200°, and distils without alteration in a stream of carbon dioxide. The vapour-density (determined at 360°) is 19·12 (calc. 18·56). The heated vapour burns in the air with a red flame and with abundant evolution of iodine. By water it is converted into silica and hydriodic acid; by absolute alcohol into silica, ethyl iodide, and hydriodic acid:

$$SiI^4 + 2C^2H^6O = SiO^2 + 2C^2H^5I + 2HI$$

(Friedel, *Ann. Ch. Pharm.* cxlix. 96).

Tri-iodide. Si^2I^6.—When silicon tetriodide is heated nearly to its boiling point (290°–300°) with finely divided silver, a white mass is obtained, which may be freed from unaltered tetriodide by repeated treatment with small quantities of carbon bisulphide, and then dissolved, with aid of heat, in a large quantity of that liquid. The solution on cooling yields the tri-iodide $Si^2I^6 =$ $\begin{array}{c}SiI^3\\ |\\ SiI^3\end{array}$ in beautiful colourless hexagonal prisms or rhombohedrons, having a single axis of double refraction, fuming and changing into a white mass on exposure to the air. When treated with potash, it yields silica, hydriodic acid, and free hydrogen, in quantities corresponding to the equation:

$$Si^2I^6 + 4H^2O = 2SiO^2 + 6HI + H^2.$$

Silicon tri-iodide cannot be distilled under either ordinary or reduced pressure. It may be partially sublimed, but decomposes for the most part into tetriodide and an orange-red residue, insoluble in carbon bisulphide, benzol, chloroform, and silicon tetrachloride, and converted by water into a white or greyish substance which eliminates a large quantity of hydrogen from potash-solution, and has nearly the composition of the di-iodide, SiI^2. The tri-iodide melts in a vacuum at about 250°, but appears to decompose partially at the same time. With ice-cold water the crystals of the tri-iodide decompose, without evolution of hydrogen, and are converted into a white mass, which after drying, first in a vacuum, and then at 100°, has the composition $Si^2H^2O^4 = Si^2\left\{\begin{matrix}(OH)^2\\ O^2\end{matrix}\right.$ or $\left.\begin{matrix}Si^2O^2\\ H^2\end{matrix}\right\}O^2$, analogous to oxalic acid. This substance when heated, decomposes with incandescence and evolution of hydrogen, leaving nearly its own weight of silica. The tri-iodide appears to be converted by water, first into $Si^2(OH)^6$, and then, by loss of $2H^2O$, in silico-oxalic acid, $Si^2H^2O^4$. Salts of this acid cannot be prepared, inasmuch as it is decomposed, with evolution of hydrogen, even by the weakest bases.

When the tri-iodide is mixed by small portions with zinc-ethyl and gently warmed, a white mass separates; and on distilling the liquid after the requisite quantity of the iodide has been added ($2Si^2I^6$ to $3(C^2H^5)^2Zn$), washing the distillate first with water, then repeatedly with strong sulphuric acid, and lastly with water again, then drying and submitting it to fractional distillation, silicon-tetrethyl passes over at 150°–154°, and at 250°–253° a liquid having the composition of silicon-triethyl, $Si^2(C^2H^5)^6$. This liquid has a faint odour, like that of silicon-tetrethyl, and burns with a luminous flame depositing silica. Vapour-density obs. = 8·5; calc. 7·96. The slight difference arises from the formation at 300° of a small quantity of a product soluble in concentrated sulphuric acid, doubtless the oxide $Si^2(C^2H^5)^4O$ (Friedel a. Ladenburg, *Compt. rend.* lxviii. 920; *Zeitschr. f. Chem.* [2] v. 289).

In the compounds just described the two atoms of quadrivalent silicon are united into a sexvalent group, just like the two atoms of carbon in the ethyl-compounds; the tri-iodide, Si^2I^6, for example, is analogous to C^2Cl^6 or C^2H^6.

SILICIC IODOFORM, $SiHI^3$, is formed in very small quantity by the action of hydriodic acid on silicon, somewhat more abundantly when the hydriodic acid gas is mixed with hydrogen. It then condenses in drops, together with the solid iodide, and may be separated from the latter, though not easily, by distillation. It is a colourless, strongly refracting liquid, of sp. gr. 3·362 at 0°, and 3·314 at 20°; boils at about 220°. It is decomposed by water in the same way as silicic chloroform. The hydrosilicic iodide described by Wöhler a. Buff (v. 274) appears to have been a mixture of silicic iodide with a very small quantity of silicic iodoform (not more than 8 p. c. of the mixture) and free iodine. The red solution of this substance in carbon bisulphide is decolorised by agitation with metallic mercury, and after the evaporation of the solvent, leaves a yellowish liquid which solidifies to a crystalline mass and distils at 285°. It dissolves in potash with evolution of hydrogen, the quantity of which however is unimportant (0·036 p. c.), and much smaller than that which corresponds to the formula $Si^3H^2I^{10}$ (0·60 p. c.); the amount of silicon agrees with the formula SiI^4 (Friedel, *loc. cit.*).

SILICIC SULPHYDRATE (chlorinated). $\left.\begin{matrix}SiCl^3\\H\end{matrix}\right\}S$. *Silicic Mercaptan.*—This compound, analogous to methyl-mercaptan, $\left.\begin{matrix}CH^3\\H\end{matrix}\right\}S$, is produced by passing a mixture of hydrogen sulphide and vapour of silicic chloride through a red-hot tube:

$$SiCl^4 + H^2S = HCl + SiCl^3HS.$$

It is a colourless liquid, boiling at 196°, smelling of hydrogen sulphide and silicic chloride, and decomposed by moist air, with formation of silica, hydrochloric acid, and sulphur. With absolute alcohol it forms normal silicic ether, $Si(OC^2H^5)^4$, the compound $Si(OC^2H^5)^3HS$ being apparently also formed as an intermediate product. Dry bromine decomposes silicic mercaptan, with rapid evolution of hydrobromic acid and formation of silicic chlorobromide, $SiCl^3Br$:

$$2SiCl^3HS + 3Br^2 = 2SiCl^3Br + Br^2S^2 + 2HBr.$$

The chlorobromide, separated by distillation from the bromine sulphide, is a colourless liquid, which fumes in the air, boils at 80°, and has a vapour-density = 7·25 (calc. 7·42). With water it is resolved into silica, hydrochloric acid, and hydrobromic acid. Silicic chlorobromide is likewise obtained by heating silicic chloroform to 100° for some time with bromine, and submitting the product to fractional distillation (Friedel a. Ladenburg, *Bull. Soc. Chim.* [2] vii. 472).

SILICOFLUORIDES. The specific gravity of potassium silicofluoride is 2·6649–2·6655 at 17·5°; of the sodium salt, 2·7547 at 17·5°; of the barium salt, 4·2741 at 21°, all referred to an equal volume of water at 15° as unity (Stolba, *J. pr. Chem.* xcvii. 503).

Potassium Silicofluoride, recently precipitated in the cold, collected on a filter, and left to itself for 24 hours, retains from 63 to 65 p. c. water; when precipitated from a hot solution, it retains 45 to 46 p. c. The gelatinous precipitate appears crystalline under the microscope, especially if moistened with a little alcohol. It is less soluble in saline solutions than in pure water: 1 pt. of the salt requires for solution 833 pts. water at 17·5°; 24,066 pts. of a solution of potassium sulphate (of 9·92 p. c.) at 17°; 125,000 of an 18·4 p. c. solution of potassium nitrate at 15°; 1735 pts. of an 8·8 p. c. solution of the same salt at 100°. Aqueous sal-ammoniac of 26·3 p. c. dissolves it more easily than a 5 p. c. solution of the same salt. Acids dissolve potassium silicofluoride more easily than water, but decompose it at the same time, usually with emission of vapours of silicon fluoride. In hydrochloric acid, however, the salt dissolves without formation of visible decomposition-products, and more abundantly in proportion as the acid is stronger. When potassium silicofluoride is ignited with 1 to 2 pts. of sal-ammoniac, ammonium silicofluoride is given off, and potassium chloride remains behind. When the potassium salt is boiled with carbonate of magnesium or calcium, in presence of water, fluoride of magnesium or calcium is formed, but the decomposition is never complete (Stolba, *J. pr. Chem.* ciii. 396; *Zeitschr. f. Chem.* [2] iv. 576).

Caesium Silicofluoride, $2CsF.SiF^4$, is prepared by precipitating cæsium chloride with cupric silicofluoride, and washing the precipitate on a filter till all the copper salts are removed; it forms anhydrous crystals. When precipitated by alcohol it is not distinctly crystalline, but from a hot solution it separates in shining octohedrons truncated by cubic faces. By spontaneous evaporation, cubes with truncated summits are obtained. Sp. gr. 3·3756 at 17°. One part of the salt dissolves in 166 pts. water at 17°, and in a much smaller quantity of hot water, but it is insoluble in alcohol. Ignited with sal-ammoniac it leaves pure cæsium chloride. It is easily and completely decomposed by lime-water (Stolba, *J. pr. Chem.* ciii. 410).

Rubidium Silicofluoride, $2RbF.SiF^4$, is precipitated from hot solutions as a distinctly crystalline powder, appearing under the microscope to consist of transparent cubes modified with octohedral and dodecahedral faces; the precipitate formed in the cold is less crystalline. Sp. gr. 3·3383 at 20° referred to water at the same temperature. 1 pt. of the salt dissolves in 614 pts. water at 20°, in 73·8 pts. at the boiling heat. The aqueous solution has an acid taste and reaction; a solution saturated at 20° has a sp. gr. of 1·0013. The salt is more soluble in acids than in water; insoluble in alcohol; reacts with alkalis like the potassium and sodium salts (Stolba, *J. pr. Chem.* cii. 1).

Cupric Silicofluoride, $CuF^2.SiF^4$, may be prepared by dissolving cupric carbonate in dilute silicofluoric acid, or by boiling barium silicofluoride with the solution of an equivalent quantity of cupric sulphate (adding a small quantity of the barium salt towards the end of the process till the sulphuric reaction disappears), and evaporating in a vacuum at 10° to 22°. It forms crystals belonging to the hexagonal system and consisting of $2(CuF^2.SiF^4) + 13H^2O$. Sp. gr. = 2·1576 at 19° referred to water at the same temperature. The crystals deliquesce in moist, effloresce in dry air, and decompose at 100°, giving off silicon fluoride. The salt is very soluble in water, 1 pt. of it dissolving in 0·428 pt. water at 17° (sp. gr. of the solution 1·6241): 1 pt. of it dissolves also at 20° in 17·7 pts. of 62 p. c. alcohol, in 150 pts. of 85 p. c. alcohol, and in 617 pts. alcohol of 92 p. c. From the saturated solution in weak spirit there separates, on heating, or on addition of an excess of the salt, or on addition of stronger alcohol, a heavy blue liquid not miscible with the solution, and consisting of cupric silicofluoride, water, and alcohol, in variable proportions: a larger addition of strong alcohol throws down a light blue powder containing less water (according to one experiment, $2CuSiF^6 + 11H^2O$). Cupric silicofluoride, on account of its easy solubility in water and weak spirit, and its property of not corroding glass in aqueous solution, may be conveniently used as a reagent, especially for precipitating alkalis from solutions not containing sulphuric acid (Stolba, *Zeitschr. f. Chem.* [2] iv. 95).

SILICO-FORMANHYDRIDE. See page 1019.

SILICONONYL ALCOHOL. See page 1020.

SILICO-OXALIC ACID. See page 1022.

SILICOPROPIONIC ACID. See page 1020.

SILK (Cramer, *Untersuchung der Seide und des thierischen Schleims*, Inaug. Diss. Zürich, 1863; *J. pr. Chem.* xcvi. 76; *Jahresb.* 1864, p. 628; 1865, p. 653).—When silk is exhausted with water in a Papin's digester six times successively for two or three hours each, under a pressure of three atmospheres (at 133°), and the pale yellow shining residue is freed from colouring matter by treatment with strong alcohol, and from a trace of fatty matter by ether, the undissolved portion, amounting to 66 p. c. of the silk, consists of **fibroïn**, $C^{15}H^{23}N^5O^6$, having the appearance of cleansed silk, and easily torn (but not pulverisable). Fibroïn boiled for some time with dilute sulphuric acid yields glycocine, together with leucine and tyrosine, the amount of the two former being about five times as great as that of the tyrosine.

Sericin or ***Silk-gelatin*** is obtained by boiling silk with water for about three hours, precipitating the expressed liquid with basic lead acetate, and decomposing the washed precipitate suspended in hot water with hydrogen sulphide. The liquid separated therefrom and somewhat concentrated, is first mixed with a quantity of alcohol just sufficient to produce a permanent precipitate, and the sericin is then precipitated from the clear filtrate by further addition of alcohol. After boiling with alcohol and ether, drying, and pulverisation, it forms a colourless, scentless, and tasteless powder, which swells up strongly in water, and dissolves in hot water more easily than ordinary gelatin. A solution containing less than 1 p. c. still coagulates on cooling to a consistent jelly, which, however, loses this property by prolonged boiling, as well as by addition of acetic acid, potash, or soda. Tannic acid produces in the solution a white thick flocculent precipitate; ferrocyanide and ferricyanide of potassium do not form any precipitate in the solution acidulated with acetic acid; aluminium sulphate and the salts of most of the heavy metals form precipitates which partly dissolve when heated, or in an excess of the precipitant.

The analysis of sericin leads to the formula $C^{15}H^{25}NO^8$, differing from that of fibroïn by addition of O and H^2O. The formation of sericin from fibroïn by oxidation is in accordance with the fact that fibroïn, after prolonged exposure to the air, becomes attackable by water; but the products of decomposition by sulphuric acid do not agree with this supposition. Sericin, in fact, when boiled for some time with a mixture of 1 vol. sulphuric acid and 4 vol. water, yields no glycocine, and only a small quantity of leucine, but, on the other hand, about 5 p. c. tyrosine and 10 p. c. of a body called **serine**, closely related to alanine.

Serine.—To prepare this substance, silk is moistened in the bag till its surface is sufficiently softened—an operation often performed in dye-works for the purpose of cleansing—and then immersed for a short time in boiling water. To obtain a sufficiently concentrated solution, several portions of silk are treated with the same quantity of water, and the liquid is evaporated till it contains from 7 to 8 p. c. sericin. It is then mixed with ¼ vol. sulphuric acid, boiled for 24 hours in a flask with upright condenser, and supersaturated with lime. The filtrate neutralised from time to time with sulphuric acid deposits on evaporation, first tyrosine and gypsum, and then serine in groups of crystals; finally a small portion of leucine crystallises from the mother-liquor. The serine, after being pressed, is dissolved for further purification in 40 pts. of cold water, and the solution filtered from tyrosine is mixed with a few drops of ammonia and ammonium carbonate to precipitate a small quantity of lime, and evaporated to the crystallising point. The last residue of green combinations of a rhombohedron with a prism of the second order (axes $a : c$ = 1 : 0·5136; angle of terminal edges = 127° 34′), and is isomorphous with the corresponding double chloride. The platinobromides of *magnesium*, *manganese*, *zinc*, and *cobalt* have the general formula $\mathrm{M''Br^2.PtBr^4 + 12H^2O}$; they are very soluble, but crystallise easily in irregularly developed rhombohedral combinations containing the same amount of water as the corresponding platinochlorides:

	Length of principal axis c of the rhombohedron (a = 1)	Terminal angle of rhombohedron
$\mathrm{MgBr^2.PtBr^4 + 12H^2O}$	0·6974	114° 12′
$\mathrm{MnBr^2.PtBr^4 + 12H^2O}$	0·7025	113° 53′
$\mathrm{ZnBr^2.PtBr^4 + 12H^2O}$	0·6989	114° 6′
$\mathrm{CoBr^2.PtBr^4 + 12H^2O}$	0·6970	114° 10′

The *calcium salt* has the same amount of water, and crystallises in small crimson ill-defined crystals.

Chlorides. When a solution of platinic chloride, freed from nitric acid by heating with hydrochloric acid, is evaporated over sulphuric acid and lime, large brown-red very deliquescent crystals are obtained, consisting of the *acid chloride*, *hydroplatinic chloride*, or *hydrogen platinochloride*, $\mathrm{H^2PtCl^6 + 6H^2O}$ or $\mathrm{2HCl.PtCl^4 + 6H^2O}$ (R. Weber, *Pogg. Ann.* cxxxi. 443).

Fuming nitric acid added to not very acid solutions of platinic chloride throws down the greater part of the platinum as a yellow precipitate, which when drained on an asbestos filter, and dried on a porous plate over sulphuric acid, forms a brownish-yellow deliquescent powder. This substance dissolves in water with evolution of nitrogen dioxide; but is decomposed by potash, with formation of nitric acid and without evolution of gas. Weber (*ibid.* 441) represents this compound by the formula $\mathrm{PtCl^4.2NO^2Cl + H^2O}$; it is probably identical with that which Boyé and Rodgers obtained (iv. 668) by evaporating platinic chloride with nitromuriatic acid.

Platinochlorides.—Topsöe (*Jahresb.* 1868, p. 273) has prepared the following platinochlorides by adding weighed quantities of the corresponding oxides or carbonates to solution of acid platinic chloride, $\mathrm{(PtCl^4.2HCl + 6H^2O)}$, and evaporating over sulphuric acid at ordinary temperatures. The *barium salt*, $\mathrm{BaCl^2.PtCl^4 + 4H^2O}$, crystallises in monoclinic prisms, $\infty P\infty . oP . \infty P . P$, sometimes tabular from predominance of the orthopinacoïds, and having the clinodiagonal, orthodiagonal, and principal axis in the proportion of 0·948 : 1 : 1·48, and the angle of the inclined axes = 77° 40′. The *calcium salt*, $\mathrm{CaCl^2.PtCl^4 + 3H^2O}$, forms light yellow, warty or laminar, somewhat deliquescent crystals. The *lead salt*, $\mathrm{PbCl^2.PtCl^4 + 3H^2O}$, crystallises in hard light yellow cubes, decomposed by a large quantity of hot water, with separation of lead chloride; according to Birnbaum, the crystals contain $\mathrm{4H^2O}$, have an orange-red colour, effloresce over sulphuric acid, but deliquesce in the air, and dissolve easily in water and in alcohol.

The platinochlorides of the magnesium group have the general formula $\mathrm{M''Cl^2.PtCl^4 + 6H^2O}$. They are very soluble—the cupric salt very deliquescent—but nevertheless crystallise with facility. The more or less yellow crystals are combinations of a rhombohedron of the first order with a prism, usually predominating, of the second order; sometimes they exhibit a monoclinic or even quadratic aspect. Topsöe describes the following:

	Length of axis c (a = 1)	Terminal angle of primary rhombohedron
$\mathrm{MgCl^2.PtCl^4 + 6H^2O}$	0·5169	127° 17′
$\mathrm{MnCl^2.PtCl^4 + 6H^2O}$	0·5310	126° 10′
$\mathrm{FeCl^2.PtCl^4 + 6H^2O}$	0·5144	127° 30′
$\mathrm{NiCl^2.PtCl^4 + 6H^2O}$	0·5162	127° 22′
$\mathrm{CoCl^2.PtCl^4 + 6H^2O}$	0·5140	127° 32′
$\mathrm{ZnCl^2.PtCl^4 + 6H^2O}$	0·5169	127° 18′
$\mathrm{CdCl^2.PtCl^4 + 6H^2O}$	0·5235	126° 46′
$\mathrm{CuCl^2.PtCl^4 + 6H^2O}$	0·5219	126° 53′

The magnesium and manganese salts crystallise in this form only above 20°; at lower temperatures, in irregularly developed combinations of two rhombohedrons with a prism of the second order; these two salts are likewise isomorphous:

	Axis c	Terminal angle
$\mathrm{MgCl^2.PtCl^4 + 12H^2O}$	0·7057	113° 40′
$\mathrm{MnCl^2.PtCl^4 + 12H^2O}$	0·7073	113° 44′

by a known volume of neutral ammonium sulphite at the boiling heat; the two liquids are mixed in the required proportions; the mixture is left at rest for 48 hours in a vessel closed air-tight, whereupon about a third part of the silver separates as a crystalline deposit; and the decanted dark blue solution is heated for some time to 60°–70°, whereby, if a sufficient excess of ammonium sulphite is present, it is completely decolorised (unless the silver contains cobalt or nickel, in which case the liquid remains red or pale green). The precipitated silver, after being washed, is digested with concentrated ammonia (a small quantity of silver then passing into solution, and remaining on evaporation as a black speculum of silver nitride), then washed and dried. To obtain it in compact form it is fused with 5 p. c. ignited borax mixed with $\frac{1}{10}$ sodium nitrate, and poured into moulds lined with a paste of ignited and unignited kaolin. The cooled bars are then cleaned with sand, ignited with pure potash (to remove the kaolin), and washed. If they have to be cut into smaller pieces with a steel chisel, the pieces must be again digested with pure strong nitric acid, and washed with ammoniacal and pure water.

Silver thus prepared, if the solution has been diluted to the degree above directed, is free from all but mere traces of volatile or oxidisable impurities. Exposed to the flame of the coal-gas and oxygen blowpipe in a crucible of burnt marble, it melts without becoming spotted; boils briskly at a higher temperature, giving out a pale blue flame (or purple from admixture of strontium, calcium, or lithium vapour from the substance of the crucible), colouring the burnt lime deep yellow, and finally volatilising without a trace of residue.

Equally pure silver may be obtained, according to Stas, by Millon a. Commaille's process of reduction with an ammoniacal solution of cuprous chloride (*Jahresb.* 1863, p. 283), provided this solution is free from iron. But a solution prepared with commercial copper always contains ferrous oxide, and therefore yields a silver precipitate containing ferric oxide, from which the iron cannot be separated by any simple process.

Gräger (*Zeitschr. anal. Chem.* viii. 64) prepares pure silver by reducing an ammoniacal solution of the chloride with excess of zinc, digesting the washed precipitate with strong hydrochloric acid, washing it with water, then with aqueous ammonia, and then again with water. Pure silver may be separated in this manner from ammoniacal solutions containing copper, provided the quantity of zinc present is less than sufficient to reduce all the silver.

When cupriferous silver is distilled as above in a kind of retort made of two pieces of burnt marble fitted one upon the other, part of the copper distils with the silver, and argentiferous copper remains in the retort, the copper for the most part as oxide. Lead is volatilised or oxidised before the silver.

Distilled silver is dazzling white, of sp. gr. 10·575, and softer than fused silver, by which it is scratched. Perfectly pure silver in very thin layers appears bluish-green by transmitted light, in somewhat thicker layers yellow to yellow-brown. Such deposits are obtained by dissolving silver in a hot solution of potassium cyanide, and when the liquid has cooled to 60°–70°, dipping into it a glass tube heated to a somewhat higher temperature. In a tube thus lined with a very thin film of silver, a mixture of chlorine and hydrogen detonates instantly in sunshine; if the coating is thicker, the combination takes place in the course of a few hours without explosion (Christomanos, *Zeitschr. f. Chem.* [2] v. 310).

Foucault (*Compt. rend.* lxiii. 413) also found that thin silver specula transmit light with bluish colour (the translucency being a property of the silver and not dependent on porosity), and that therefore plane glasses or lenses silvered on one side might be used in optical instruments for diminishing the intensity of light.

Soulié (*Bull. Soc. Chim.* [2] viii. 136) describes a process now used in the United States for extracting gold and silver from their ores, which consists in forcing the finely pulverised and moistened ore (pyriteferous or quartzose) through melted lead by atmospheric pressure. The gold and silver, as well as the metallic oxides and sulphides, are taken up by the lead, while the exhausted ore rises to the surface, and is removed by a peculiar arrangement. The lead when sufficiently charged with gold or silver is expelled.

W. G. Blagden (*Mechanic's Magazine*, Sept. 1867, p. 220; *Jahresb.* 1867, p. 887) describes a method of desilvering lead by means of zinc and the electric current. The previously refined metal is heated to 450° in a pan like those used in Pattinson's process, about $\frac{1}{2}$ p. c. zinc is added, and as soon as it is completely dissolved, an electric current is passed into the bath by means of copper wires for 10 to 30 minutes. The zinc holding the silver in solution then rises to the surface, and may be removed as a solid crust when the bath has cooled to about 450°. For satisfactory desilverisation (down to $\frac{1}{500}$ p. c.) the operation must be repeated several times.

On the action of light on *chloride, bromide,* and *iodide of silver*, see Poitevin, *Bull. Soc. Chim.* [2] v. 155;—Kaiser, *Jahresb.* 1865, p. 279;—Carey Lea, *Sill. Am. J.* [2] xxxix. 74; xl. 109; xlii. 198; *Jahresb.* 1865, pp. 279, 282; 1866, p. 262;—H. Vogel, *Pogg. Ann.* cxxv. 329;—W. Reissig, *J. pr. Chem.* xcv. 405;—Schultz-Sellack, *Deut. chem. Ges. Ber.* iv. 210; *Chem. Soc. J.* [2] ix. 302. According to Lea, pure silver iodide is not reduced by light, the reduction taking place only in presence of silver nitrate or organic bodies.

Silver Fluoride. AgF.—This compound has been carefully examined by Gore (*Phil. Trans.* 1870, 227; *Proc. Roy. Soc.* xix. 235). It was prepared by dissolving pure silver carbonate in hydrofluoric acid and evaporating in a platinum dish, but, unless peculiar precautions are taken, it generally contains a little metallic silver and traces of water and hydrofluoric acid. It is usually obtained in yellow earthy lumps, but when completely dehydrated by fusion, it forms a black horny mass, having a silvery lustre on the surface, arising from minute particles of metallic silver. It is extremely deliquescent; 1 pt. of it dissolves in 0·55 pts. water at 15·5°, heat being evolved in the dissolution, and a strongly alkaline liquid being formed. The saturated solution has a sp. gr. of 2·61 at 15·5°, exhibits supersaturation on cooling, and solidifies, with rise of temperature, when a platinum plate is dipped into it. Crystals of a hydrated salt may be obtained from the solution, but the rest of the salt separates at the same time in the anhydrous and amorphous state. The dry salt is not decomposed by light. It melts below a visible red heat, forming a strongly lustrous, mobile, pitch-black liquid. It is not decomposed by heat alone, but in the fused or semifused state it is quickly decomposed by the moisture of the air, with separation of metallic silver; dry air does not affect it. Brought in contact in the fused state with platinum poles, it conducts electricity like a metal, without visible evolution of gas or corrosion of the positive pole; a silver pole is quickly dissolved, and a carbon pole gradually attacked. The aqueous solution yields by electrolysis, silver crystals at the negative, and silver peroxide at the positive pole. Hydrogen does not affect the dry salt in sunshine, but decomposes it gradually at a commencing red heat, with separation of metallic silver. The dry salt and the aqueous solution are not decomposed by oxygen or by nitrogen; neither do the oxides of nitrogen act on the fused salt. Ammonia gas is quickly absorbed by the dry and by the fused salt, in the latter case with separation of metallic silver; the concentrated solution is also decomposed by strong aqueous ammonia. When vapour of hydrofluoric acid is passed over the perfectly dry and previously fused salt, at a temperature of 13°, an acid fluoride is formed, which however decomposes at a slightly higher temperature.

When silver fluoride is heated in chlorine gas, in vessels constructed partly of glass, partly of platinum, the glass is more or less attacked, the chlorine unites with the platinum and the silver fluoride, forming a double salt, $4AgCl.PtF^4$, and a vacuum is produced. Similar results are obtained in vessels of platinum alone or of gold. In vessels constructed partly of purified graphite a compound of fluorine and carbon is formed. Bromine and iodine act upon silver fluoride in a similar manner; iodine however does not form a double salt analogous to the chlorine-compound above mentioned. An aqueous solution of silver fluoride agitated with chlorine becomes hot and gives off oxygen:

$$8AgF + Cl^8 + 4H^2O = 7AgCl + AgClO^3 + 8HF + O.$$

Dry hydrochloric acid gas completely decomposes silver fluoride in the melted state, but only acts upon it superficially at 60° F. A saturated aqueous solution of silver fluoride is not precipitated by chloric acid.

Silver Oxides. *Argentous Oxide*, Ag^4O, is produced by the action of hydrogen dioxide on metallic silver (and therefore also in the decomposition of argentic oxide by excess of hydrogen dioxide). A bright silver plate immersed in a perfectly neutral solution of hydrogen dioxide becomes covered with bubbles of oxygen and coated with a greyish-white film, while part of the silver is converted by addition into hydrated argentous oxide, according to the equation $2Ag^2 + H^2O^2 = 2HAg^2O$, and dissolves in the liquid; a small quantity of a grey-black precipitate is likewise deposited. The solution of argentous hydrate when exposed to the air acquires the colour of cobaltous salts, and becomes slightly clouded by separation of finely divided silver. With potash it forms a brown-black precipitate; with hydrochloric acid a precipitate of silver chloride and metallic silver: $2HAg^2O + 2HCl = 2H^2O + 2AgCl + Ag^2$. When evaporated it leaves a residue which appears crystalline under the microscope, and when treated with water gives up argentic hydrate and deposits metallic silver in transparent, red, microscopic crystals, according to the equation $2HAg^2O = 2HAgO + Ag^2$;

the solution of argentic hydrate thus obtained has a slight alkaline reaction, and gives with hydrochloric acid a precipitate of silver chloride (Weltzien, *Ann. Ch. Pharm.* cxlii. 105).

On the preparation of *silver peroxide* by electrolysis of an aqueous solution of the nitrate, see Böttger, *Zeitschr. f. Chem.* [2] vi. 82.

Decomposition of Organic Silver-salts by Water.—When silver malate is boiled with water till only traces of silver remain in solution, the liquid freed from these traces yields on evaporation nothing but malic acid. The tartrate similarly treated yields only tartaric acid; the vapours given off during the boiling of this salt have an acid reaction, and when neutralised with baryta-water yield barium-carbonate, together with small quantities of a barium salt which crystallises in acuminated needles (Kämmerer, *Ann. Ch. Pharm.* cxlviii. 237).

SINCALINE. From experiments by Claus a. Keesé (*J. pr. Chem.* cii. 24; *Jahresb.* 1867, p. 494), this base appears to be identical with neurine or choline.

SITESIN. The name applied by Commaille (*J. Pharm.* [4] iv. 108) to the casein of gluten.

SITOSIN. Commaille's name for the albumin of wheat-flour.

SODA. For the continuation of Kolb's researches on the soda-manufacture and the composition of soda-waste, see *Ann. Ch. Phys.* [4] viii. 135; x. 106; *Bull. Soc. Chim.* [2] vii. 370; *Jahresb.* 1866, p. 850; *Chem. News*, xiii. 162; xiv. 16, 40, 55. See also Petersen, *Bull. Soc. Chim.* [2] viii. 35; *Jahresb.* 1866, p. 853;—Weldon, *Chem. News*, xiv. 41;—Scheurer-Kestner, *Ann. Ch. Phys.* [4] xi. 220; *Bull. Soc. Chim.* [2] vii. 217; *Jahresb.* 1867, p. 904;—Hargreaves, *Chem. News*, xv. 219, 232; *Jahresb.* 1868, p. 931;—Wright, *ibid.* xvi. 17; *Chem. Soc. J.* [2] v. 407;—Brisse, *Bull. Soc. Chim.* [2] vi. 100, 134;—Kessler, *ibid.* 299; *Jahresb.* 1867, p. 907;—Schlösing a. Rolland, *Ann. Ch. Phys.* [4] xiv. 5;—Ungerer, *Dingl. pol. J.* clxxxviii. 140; *Bull. Soc. Chim.* [2] x. 160; *Jahresb.* 1868, p. 932.

SODIUM. This metal, together with the rest of the alkali-metals, has hitherto been regarded as monatomic or univalent. Wanklyn, however, from considerations relating to the composition and reactions of sodium-ethylate and other organic sodium-compounds, concludes that it is in most cases trivalent, sometimes also quinquivalent or septivalent, and possibly capable of exhibiting still higher degrees of combining capacity.

Crystallised sodium ethylate, or sodium alcohol, obtained by the action of sodium on absolute alcohol, has the composition $C^2H^5NaO.3C^2H^6O$, and when heated to 200° for some time gives off 3 mol. alcohol and leaves a white amorphous residue consisting of absolute sodium ethylate, C^2H^5NaO, or ethylene-sodium hydrate, C^2H^4NaOH (p. 593). To these two compounds Wanklyn assigns the following formulæ:

$$Na''' \left\{ \begin{array}{l} (C^2H^4)'' \\ OH \end{array} \right.$$

or

$$Na''' \left\{ \begin{array}{c} (C^2H^4)^{iv} \\ | \\ O \\ H \end{array} \right. \qquad Na^{vii} \left\{ \begin{array}{l} OC^2H^5 \\ H \\ OC^2H^5 \\ H \\ OC^2H^5 \\ H \\ OC^2H^5 \end{array} \right.$$

Absolute. Crystallised.

Ethylene-sodium hydrate is capable of uniting directly with hydrogen chloride, hydrogen sulphide, and acetyl chloride, forming compounds represented by the formulæ:

$$Na''' \left\{ \begin{array}{l} (OC^2H^5)' \\ H \\ Cl \end{array} \right. \qquad Na''' \left\{ \begin{array}{l} (OC^2H^5)' \\ H \\ (SH)' \end{array} \right. \qquad Na''' \left\{ \begin{array}{l} (OC^2H^5)' \\ C^2H^3O \\ Cl \end{array} \right.$$

With ethyl acetate it forms ethylene-sodium acetate and alcohol:

$$Na''' \left\{ \begin{array}{l} C^2H^4 \\ OH \end{array} \right. + \left\{ \begin{array}{l} C^2H^3O \\ OC^2H^5 \end{array} \right. = Na''' \left\{ \begin{array}{l} C^2H^4 \\ OC^2H^3O \end{array} \right. + HOC^2H^5.$$

Corresponding compounds containing the radicles valeryl and benzoyl are obtained in like manner. Sodium amylate or amylene-sodium hydrate, obtained by the action of sodium on amyl alcohol, likewise yields similar salts, *e.g.* the valerate

$$Na''' \left\{ \begin{array}{l} C^5H^{10} \\ OC^5H^9O. \end{array} \right.$$

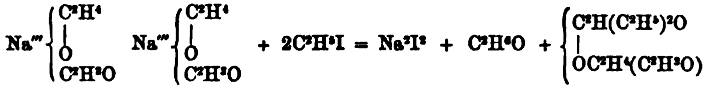
All these salts when treated with water yield ethylic or amylic alcohol, and an acetate, valerate, &c. : *e.g.*,

$$Na'''\left\{\begin{array}{l}C^2H^4\\ OC^2H^3O\end{array}\right. + H^2O = C^2H^6O + NaOC^2H^3O.$$

The preceding compounds might of course be represented by formulæ containing univalent sodium : *e.g.*,

$$\text{Ethylene-sodium hydrate, } C^2H^4\left\{\begin{array}{l}Na'\\ OH\end{array}\right..$$

But Wanklyn suggests that if sodium alcohol really had this constitution, that is to say, if it consisted of ethyl alcohol in which an atom of hydrogen in the ethyl-radicle was replaced by sodium, it should admit of the replacement of its sodium in that radicle by ethyl (*e.g.* when treated with ethyl iodide), and yield hydrate of ethylated ethyl, that it to say hydrate of butyl, or butylic alcohol. In like manner ethylene-sodium acetate, if it consisted of sodinated ethyl acetate, $C^2H^4Na.OC^2H^3O$, should be converted by similar treatment into ethylated ethyl acetate or butyl acetate. But neither of these transformations is observed to take place. The acetate treated with ethyl iodide undergoes, in fact, a more complicated decomposition, yielding sodium iodide, alcohol, and acetylinated ethyl caproate; thus :



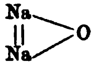
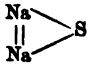
$$\underset{\text{2 mol. Ethylene-sodium acetate.}}{Na'''\left\{\begin{array}{l}C^2H^4\\ \vert\\ O\\ C^2H^3O\end{array}\right. \quad Na'''\left\{\begin{array}{l}C^2H^4\\ \vert\\ O\\ C^2H^3O\end{array}\right.} + 2C^2H^5I = Na^2I^2 + \underset{\text{Alcohol.}}{C^2H^6O} + \underset{\text{Acetylinated ethyl caproate.}}{\left\{\begin{array}{l}C^2H(C^2H^5)^2O\\ \vert\\ OC^2H^4(C^2H^3O)\end{array}\right.}$$

The trivalent character of sodium is further exhibited in sodium-triacetyl, $Na'''(C^2H^3O)^3$, produced, together with ethylene-sodium acetate, by the action of sodium on ethyl acetate (p. 15) :

$$Na^4 + 3(C^2H^5OC^2H^3O) = Na(C^2H^3O)^3 + 3Na'''\left\{\begin{array}{l}C^2H^4\\ OH\end{array}\right.,$$

and in the double compound of sodium-ethyl and zinc-ethyl, $Na'''\left\{\begin{array}{l}(ZnC^2H^5)'\\ C^2H^5\\ C^2H^5\end{array}\right..$

The inorganic compounds of sodium may also be represented by formulæ containing trivalent sodium : *e.g.*,

Hydrate. . .	$Na\left\{\begin{array}{l}O''\\ H\end{array}\right.$	Chloride . .	$\begin{array}{l}NaCl\\ \Vert\\ NaCl\end{array}$
Sulphydrate .	$Na\left\{\begin{array}{l}S''\\ H\end{array}\right.$	Oxide . . .	 $\begin{array}{l}Na\\ \Vert\\ Na\end{array}\!\!>O$
Nitrate . . .	$Na\left\{\begin{array}{l}O''\\ NO^2\end{array}\right.$	Sulphide . .	 $\begin{array}{l}Na\\ \Vert\\ Na\end{array}\!\!>S$
Acetate . . .	$Na\left\{\begin{array}{l}O''\\ C^2H^3O\end{array}\right.$	Amide . .	$Na\left\{\begin{array}{l}(NH)''\\ H\end{array}\right.$
Hypochlorite .	$Na\left\{\begin{array}{l}O''\\ Cl\end{array}\right.$	Sodio-mercuric iodide . .	$Na\left\{\begin{array}{l}(HgI)'\\ I\\ I\end{array}\right.$
Bleaching soda	$Na\left\{\begin{array}{l}(OCl)''\\ H\\ Cl\end{array}\right.$	Sodio-platinic chloride .	$\begin{array}{l}NaCl^2\\ \vert\\ (PtCl^2)''\\ \vert\\ NaCl^2\end{array}$
Sulphate . .	$\begin{array}{l}Na\equiv O\\ \vert\\ (SO^2)''\\ \vert\\ Na\equiv O\end{array}$		
Acid sulphate	$\begin{array}{l}Na\equiv O\\ \vert\\ SO^2\text{—}OH\end{array}$		

This list might be indefinitely extended, so as to include a host of double chlorides, bromides, and iodides, which, on the usual hypothesis of the monad character of sodium, are regarded as 'molecular compounds,' that is to say, as compounds whose structure we are not yet able to explain.

Precisely similar views may be taken of the constitution of the compounds of potassium and of the other alkali-metals. For further details, see *Ann. Ch. Pharm.* cli. 200; *Chem. News*, xx. 293, 313; xxi. 97.

Metallic sodium is not acted on by *chlorine gas*, either when it has been previously fused, or when agitated in the fused state with the gas (Wanklyn, *Chem. News*, ix. 271).

SODIUM-AMALGAM. See AMALGAMS, under MERCURY (p. 816).

SOLANINE. According to Kletzinsky (*Zeitschr. f. Chem.* [2] ii. 127), this base has the composition $C^{21}H^{35}NO^{7}$, and in contact with sodium-amalgam is resolved into nicotine and butyric acid; it likewise yields nicotine when fermented with putrid cheese, sugar, and chalk.

SOMBRERITE. S. Haughton (*Phil. Mag.* [4] xxxii. 220) found in this mineral:

SiO^2	$P^2O^8Ca^3$	CO^3Ca	KCl	CaF^2	H^2O	
0·08	89·64	5·0	2·81	0·10	0·60	= 98·23

SPARTAITE. A specimen of this mineral from Sterling, Sussex County, New Jersey, analysed by C. U. Shepard (*Sill. Am. J.* [2] xxxix. 174), gave 13·79 p.c. MnO, 43·65 CaO, and 42·01 CO^2, agreeing with the formula $(\frac{1}{5}MnO, \frac{4}{5}CaO).CO^2$. Sp. gr. 2·815. To avoid confusion with the red zinc-ore called *spartalite* (v. 356), Shepard proposes to designate this calcio-manganous carbonate as *calcimangite*.

SPECTRAL ANALYSIS. *Applications to Terrestrial Chemistry.*—The only exception to the general fact that incandescent solids emit light of every degree of refrangibility has been observed by Bunsen (*Ann. Ch. Pharm.* cxxxvii. 1) in the case of glowing erbia, which gives a broken spectrum in which the bright lines are intense enough to serve as a means of detecting this rare earth. This singular phenomenon does not however constitute an exception to the law of exchanges; for Bunsen has shown that the bands of maximum intensity in the emission spectrum coincide exactly in position with the bands of greatest darkness in the absorption spectrum. A similar inversion of the didymium bands has also been observed by Bunsen. The same observer has published some interesting facts respecting the absorption spectrum of the erbium and didymium compounds when examined by polarised light (*Phil. Mag.* [1866] xxxii. 177). From these experiments it appears that the absorption-bands vary slightly, (1) according to the chemical nature of the particular salts of these metals employed, and (2) according as the ordinary or the extraordinary ray is allowed to pass through the crystal. A variation in these absorption-bands is also noticed according to the direction which the ray is passed through the crystal of sulphate, and again a difference is perceived in the nature of the absorption-band thus produced and those caused by absorption in a solution of the salt.

'These differences,' says Bunsen, 'observed in the absorption spectra of different didymium compounds cannot, in our complete ignorance of any general theory of the absorption of light in media, be connected with other phenomena; they remind one of the slight gradual alteration in pitch which the notes from a vibrating elastic rod undergo when the rod is weighted, or of the change of tone which an organ-pipe exhibits when the tube is lengthened.'

Sorby found that certain specimens of zircon exhibit distinct absorption-bands (*Chem. News*, xix. 121), and concluded that these were caused by the presence of a new metal, to which he gave the name of jargonium. More recently, however, he has found that the peculiar spectra are due to the presence of certain compounds of uranic oxide with zirconia. (See ZIRCON.)

Crookes (*Proc. Roy. Soc.* xvii. 448) describes the spectra obtained by transmitted and reflected light from different varieties of opal; the absorption spectra exhibit dark bands identical in position with the bright lines obtained by reflection; both sets of lines show an irregular form, giving occasionally a spiral appearance, due probably to some irregularity in the cracks or laminæ causing the interference-colours.

Our knowledge of the spectra of the metals has recently received an important addition from Thalén, who has carefully mapped the bright lines of the following rare metals: glucinum, zirconium, erbium, yttrium, thorinum, uranium, titanium, tungsten, molybdenum, vanadium (*Nova Acta Reg. Soc. Upsal.* ser. iii. vol. vi. [1868]). The same observer has also determined the wave-lengths of the principal lines of *forty-five* metallic and non-metallic elements (*loc. cit.*).

The subject of the spectra of the metalloïds (see Dictionary, vol. v. 388) has attracted much attention, and the difficulty of truly explaining the results is shown by the diversity of opinions respecting the nature of the double spectra. Thus Ångström (*Spectre normal du Soleil*, Upsala, 1868, p. 38; also *Phil. Mag.* [4] xlii. 395) states that the conclusions deduced by Plücker and Hittorf (Dictionary, v. 388) regarding the double spectra which many of the metalloïds exhibit are not warranted, and that experiments made by him in conjunction with Thalén in no way bear out the opinion that one element can give totally different spectra. According to Ångström, 'the very reverse of this is true; that by successively augmenting the temperature we find that the intensity of the rays varies in a most complicated manner, and that accordingly even new rays can make their appearance if the temperature be sufficiently raised. But independently of all these mutations the spectrum of each substance always preserves its original character.' On the other hand, Frankland and Lockyer (*Proc. Roy. Soc.* xvii. 288, 453), Wüllner (*Pogg. Ann.* Dec. 1868; *Phil. Mag.* [4] xxxvii. 405), and Salet (*Phil. Mag.* [4] xlii. 318) describe certain important modifications which the spectra of hydrogen, nitrogen, and other metalloïds undergo when the tension of the gas through which the spark passes is changed, and the temperature of the particles is thereby altered. Under certain conditions of temperature and pressure the hydrogen spectrum can be reduced to one line in the green, corresponding to the solar line F, whilst the complicated spectrum of nitrogen can likewise be reduced to one bright line in the green, with traces of other more refrangible faint lines (Frankland and Lockyer). The same phenomenon with respect to nitrogen had previously been observed by Huggins (*Phil. Trans.* 1868, p. 529; Roscoe's *Spectrum Analysis*, 2nd edit. 332). Wüllner fully describes the variation of the hydrogen spectrum with the pressure; when the tension of the gas is 135 mm. the tube shines with a white light of insufficient intensity to yield a visible spectrum; when the pressure is reduced to 100 mm. the light emitted is bluish-white, and gives a continuous spectrum, in which the lines H α [C] and H β [F] stand out. Under a pressure of 70 mm. the light is reddish-white, and the spectrum is continuous with H, α, β, and α, visible, and also a series of beautifully shaded bands in the greenish and reddish yellow. This spectrum becomes more brilliant as the pressure diminishes to 30 mm. Under 21 mm. the lines H, α, β, and γ stand out brilliantly, and the shaded bands with the continuous spectrum become less intense. When the pressure is diminished to about 8 mm. the bands disappear and the continuous spectrum becomes almost invisible; under further rarefaction to 3 or 2 mm. the characteristic lines retain the same brightness, and everything else disappears almost entirely from the spectrum; yet with a simultaneous enfeeblement of the bright lines, part of the continuous spectrum reappears in the green. Hence it appears probable that the band spectrum of hydrogen belongs to a lower temperature than that in which the three lines alone are seen. The reappearance of the continuous spectrum with great rarefaction also bears out this hypothesis, inasmuch as the intensity of the current, and therefore the heating effect on the particles, diminishes by the greatly increased resistance of the highly rarefied gas. According to Wüllner, a still more remarkable change occurs when the hydrogen-tube is exhausted to the extreme limit of a Sprengel's pump; the light then suddenly becomes of a splendid green, like the light of a thallium flame, and the spectrum is quite changed. The line H α can scarcely be seen, and six splendid green lines appear on an almost black ground. This spectrum is always exhibited when the tube has attained the extreme degree of rarefaction of the Sprengel's pump, and if the discharge be continued for some time with the tube stop-cock closed, a continuous spectrum appears, but this on again exhausting (although no change of density in the gas occurs) yields the peculiar line spectrum just described. Wüllner has compared this spectrum with that of aluminium (of which metal the electrodes were composed), mercury, and other substances, traces of which might be present and might possibly cause the appearance observed, but he concludes from the non-coincidence of the green lines with those of the metals, &c., that these former are really due to hydrogen. Wüllner concludes that difference of temperature must in the case of hydrogen be regarded as the cause of the essentially different spectra observed, and hence that the emissive power of a substance may materially alter with the temperature. A similar series of observations have been made by Wüllner with oxygen; three distinct spectra may be obtained with induction-currents according as the oxygen in the tube has a greater or less density, and these three different spectra depend upon the temperature to which the particles of the oxygen are heated.

The comportment of nitrogen appears to be somewhat different; this gas furnishes two spectra, but these cannot be obtained one from the other by a simple change of density of the gas, the difference in temperature thus produced being insufficient to change the spectrum, and this can only be effected by an alteration in the mode of discharge, such as the introduction of a Leyden jar. The singular fact of the thickening or broadening of the hydrogen lines, and especially of the line H β [F], under certain conditions, was observed by Plücker, but Frankland and Lockyer concluded that this was due to diminution of pressure, 'and not appreciably, if at all, to temperature *per se*.'

In a recent communication (*Compt. rend.* Aug. 7, 1871) Ångström reasserts his conclusion that hydrogen and oxygen have each but one spectrum, that of hydrogen being the one found in the light of the sun and stars. He bases his opinion on the difficulty of obtaining any gas perfectly pure in an extreme state of rarefaction; thus on one occasion he rarefied air in a Geissler's tube as much as possible by a mercurial pump, causing the discharge of a Ruhmkorff's coil to pass through the tube, and obtained in succession the following spectra: (1) the ordinary air spectrum, (2) the fluted spectrum of nitrogen, (3) that of carbonic oxide, (4) the lines of chlorine and sodium. If the vacuum has been produced by mercury, the spectrum of this metal may be obtained; and if the gases are dried by sulphuric acid, the sulphur spectrum may make its appearance. Ångström then proceeds to criticise Wüllner's four different hydrogen spectra. One of these is the true hydrogen spectrum of fine bright lines, and this does change into one consisting of bright bands or into a continuous spectrum (as Ångström himself discovered in 1853) when a denser gas is used. The other two hydrogen spectra Ångström disposes of by showing that the spectrum of acetylene as observed by Berthelot is identical with one, whilst the other is identical with the sulphur spectrum.

As regards the two new spectra of oxygen found by Wüllner, Ångström shows that the lines of the one are identical with those of the oxide of carbon spectrum, whilst the other is beyond doubt the same as that of chlorine. Hence he concludes that we do not know as yet any other spectrum of oxygen beyond that discovered by himself in 1853, and examined with care by Plücker. The variation observed in the spectra of certain gases by the action of magnetism, Ångström ascribes, not to the existence of different spectra for one substance, but to the production by the magnetisation of new combinations or new substances, an action similar to that produced by inserting a condenser or Leyden jar in the circuit. Thus a Geissler's tube gave between the poles of an electromagnet the ordinary spectrum of carburetted hydrogen, whereas without the intervention of magnetism it gave the carbonic oxide spectrum without the hydrogen lines being visible; whilst another tube containing hydrogen obtained from water and dried over sulphuric acid, which gave Plücker's two hydrogen spectra, gave when under the influence of magnetism, the sulphur lines, which Wüllner believes to be a new hydrogen spectrum, whilst at the same time the carbonic oxide lines were seen near the poles.

Salet (*Compt. rend.* 1871, No. 9) has examined the spectrum of sulphur, and confirms Plücker's original discoveries, inasmuch as he concludes that two spectra of this metalloïd really exist, one composed of lines and the other of bands, the first produced by the disruptive discharge, and the second by discharges of less tension.

Under certain conditions incandescent gases can, as we have seen, yield continuous spectra. Dibbits (*Pogg. Ann.* cxii. 497) in 1864 showed that the oxyhydrogen flame yields a faint continuous spectrum, in which the bright lines of hydrogen and oxygen are not seen. And Frankland (*Proc. Roy. Soc.* xvi. 419) has proved that when the pressure under which the gases are burnt is much increased, a very considerable augmentation of the luminosity is obtained and a bright continuous spectrum is observed. A continuous spectrum is likewise obtained when many gases or vapours undergo combustion, and these considerations have led Frankland to conclude that the ordinary explanation given by Davy of the luminosity of flame is incorrect, and that the light is due, not to the incandescence of solid carbon, but to the combustion of highly condensed gaseous hydrocarbons.

It is to be remembered that although, under the conditions most generally met with, gases have been found to give discontinuous spectra, the Theory of Exchanges, upon the truth of which the science of spectrum analysis is founded, does not give us any information whether a gas yields a continuous or a broken spectrum. According to this theory, if a glowing gas absorbs some of each of the rays which fall upon it, it *must* emit a continuous spectrum. Even under diminished pressure many gases exhibit a continuous spectrum, as is seen in a flame coloured by soda or potash salt. Kirchhoff showed many years ago that when the temperature or density of a glowing gas is increased, and the luminosity of the spectrum becomes greater, the dark portions of the spectrum *must* increase in luminosity more rapidly than the bright portions. Hence it does not appear surprising that by increase of temperature and pressure the spectrum originally consisting of bright lines or bands upon a scarcely visible continuous background should by degrees change into a spectrum exhibiting all the colours in equal intensity. H. St. Claire Deville (*Phil. Mag.* [4] xxxvii. 111) gives a somewhat similar explanation of the continuous spectra from incandescent gases, and does not endorse Frankland's conclusions concerning the source of luminosity of the candle-flame.

Atmospheric Lines and Spectra of the Moon and the Planets.—The existence of dark bands caused by atmospheric absorption was first pointed out by Brewster in 1833.

In 1865–6, J. P. Cooke junior (*Proc. Amer. Acad. Sc.* vii. Jan. 1866; and *Am. Journ. Sc. and Arts*, vol. xi. Nov. 1865) showed that many of the air lines are solely due to aqueous vapour contained in the atmosphere. Janssen produced these lines artificially by allowing the light from 16 jets of coal gas to pass through a column of high-pressure steam 37 metres in length. Groups of dark lines then appear in the spectrum between the extreme red and the lines D. These lines are found to coincide with lines in the solar spectrum which become intense when the sun is near the horizon. (For Janssen's map of these lines see Roscoe's *Lectures*, 2nd edition, p. 226.)

The Moon.—No signs of a lunar atmosphere presented themselves in a most accurate examination which Mr. Huggins made as follows: the spectrum of a star was carefully observed at the moment the dark edge of the moon passed over it. If an atmosphere existed in the moon, the observer would see the starlight by refraction after the occultation had occurred, and the red rays being less refrangible would disappear before the blue. All the differently coloured rays were found to disappear at the same instant, and hence the absence of a lunar atmosphere is to be inferred.

The Planets.—In the spectrum of Jupiter, lines are seen indicating an absorptive atmosphere about this planet. One strong band corresponds to a known elementary substance (hydrogen), whilst the same conclusion is arrived at with Saturn. Padre Secchi concludes from his own observations that in all probability the vapour of water exists in the planetary atmospheres. The red colour which distinguishes Mars is not derived from absorption in its atmosphere, as the light reflected from its polar regions is free from the red tint peculiar to the other portions of the planet (Huggins, *Monthly Notices R. A. Soc.* xxvii. 178).

Spectrum of Uranus.—Huggins (*Proc. Roy. Soc.* xix. 488) has observed the absorption-spectrum of the planet Uranus with his equatorial refractor of 15-inch aperture. This is characterised by six remarkably strong absorption-lines; the strongest of these has a wave-length of about 544 millionths of a millimetre; another at 572 is nearly as broad, but not so dark; the one a little less refrangible than D is narrower than the others. The most refrangible band is identical in position with the F line, and was proved to be coincident with the bright hydrogen line F, so that this band in the planet spectrum is probably due to hydrogen. Three of the bands were found not to differ greatly in position from the bright air lines, but there is no strong line in the spectrum of Uranus corresponding to the strongest of the air lines, viz. the double nitrogen line. The lines due to carbonic acid do not appear in the Uranus spectrum; there is no absorption-band in the position of the sodium line, nor are the lines in the spectrum of Uranus at the positions of the principal groups produced by absorption in the terrestrial atmosphere.

Terrestrial Atmospheric Absorption.—Lieut. J. H. Hennessey (*Proc. Roy. Soc.* xix. 1) has mapped on a more complete scale than has been hitherto done, the absorption-lines seen at Mussoorie in India when the sun is low. An accurate map of these lines from A to D accompanies the paper, many of which are found to be identical with the air lines mapped by Kirchhoff.

Spectroscopic Observations of the Sun.—A complete memoir on the 'Normal Solar Spectrum' (Upsala, 1868) has been published by A. J. Ångström of Upsala, accompanied by an atlas of six plates exhibiting the whole length of the solar spectrum from A to H. The positions of these lines are mapped according to their wave-lengths, which have been calculated from observations most carefully made with diffraction-spectra. The bright metal lines coincident with those of Fraunhofer are also given. The following table gives a summary of the solar lines shown on Ångström's maps as produced by known elements:

Substances	No. of Lines	Substances	No. of Lines
Hydrogen . .	4	Manganese . .	57
Sodium. . .	9	Chromium . .	18
Barium . .	11	Cobalt . . .	19
Calcium . .	75	Nickel . . .	33
Magnesium . .	4+3 (?)	Zinc . . .	2 (?)
Aluminium . .	3 (?)	Copper. . .	7
Iron . . .	450	Titanium . .	118

The presence of titanium in the solar atmosphere was discovered by Thalén. Many of these lines were formerly supposed to be due to calcium, having been obtained by the ignition in the electric arc of gas carbon impregnated with calcium chloride. The carbon however contained titanium, and 118 out of 170 of the observed titanium lines were seen to be coincident. Hence there can be very little doubt as to the existence of titanium in the solar atmosphere, and the well-known occurrence of this metal in meteoric stones seems to support the view that titanium possesses a general cosmical distribution. The total number of coincident solar lines now observed amounts to close upon 800, and this number might easily be increased by using more powerful means of raising the temperature of the substance under examination. Nevertheless, the number already mapped suffices to show that, to account for the origin of all the more prominent rays in the solar spectrum, we must assume that the substances constituting the chief mass of the sun are without doubt the same bodies as exist on our planet (Ångström).

Discoveries in Solar Physics made by means of the Spectroscope.—Since the publication of the last volume of this Dictionary, discoveries have been made with respect to the sun, second only in importance to Kirchhoff's original discovery; and the subject has been so largely developed that it is impossible in the present article to do more than refer to the most striking discoveries, leaving the reader to obtain further information from works specially devoted to spectroscopic astronomy. About five years ago J. Norman Lockyer (*Proc. Roy. Soc.* Oct. 11, 1866) suggested that it might be possible by the use of the spectroscope to obtain evidence of the presence of the red prominences which total eclipses have revealed to us in the solar atmosphere, although they escape all other means of observation on other occasions. After many fruitless attempts, Mr. Lockyer at last succeeded (Oct. 20, 1868) in seeing the prominences and in ascertaining the existence of three bright lines in the following positions: I. Absolutely coincident with C. II. Nearly coincident with F. III. Near D. These bright lines were rendered visible under the ordinary condition of the sun by employing a powerful spectroscope giving very large dispersion. The almost continuous spectrum given out by the limb of the sun was thus spread out until it became very feeble, whilst the luminous intensities of the monochromatic rays given out by the glowing gas were but slightly diminished, and thus the light from the prominences became visible without being interfered with by that emanating from the body of the sun.

M. Janssen, who was sent by the French Government to Guntoor in India to observe the total eclipse on August 18, 1868, saw and measured the position of these bright lines on that day, and, struck by their intensity, he likewise conceived the idea that they might be visible when the sun was uneclipsed. On the next day he succeeded in his endeavour, 'so that,' he writes, 'I have been working for the last seventeen days in a perpetual eclipse.' The announcement of this separate discovery was received by the French Academy on October 26, 1868, a few days after Mr. Lockyer's discovery was made known to the Royal Society. By employing a wide slit with an absorption-screen of ruby glass, Huggins (*Proc. Roy. Soc.* xvii. 302) succeeded (Feb. 13, 1869) in viewing a solar prominence so as to distinguish its form, and Mr. Lockyer finds that no absorptive medium is needed. Lockyer's investigations have not only shown that the red prominences are due to incandescent hydrogen, but that the whole body of the sun is enveloped in a glowing gaseous medium extending for 5000 miles in height, of which the prominences are only local aggregations.* This envelope he terms the *Chromosphere*, to distinguish it from the cool absorbing atmosphere on the one hand and the light-giving photosphere on the other. Under proper instrumental and atmospheric conditions the spectrum of the chromosphere is always visible in every part of the sun's periphery. The bright line identical in position with Fraunhofer's phosphorus di-iodide, pouring the mixture at the termination of the reaction into water, agitating with ether, and evaporating the ethereal solution. The acid then remains in the form of an oil nearly insoluble in water, whereas β iodopropionic acid, obtained by the action of hydriodic acid or of phosphorus iodide on glyceric acid (iv. 733), crystallises easily and well (Wichelhaus, *loc. cit.*).

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* The existence of a coloured red atmosphere surrounding the sun appears to have been first observed by Grosch during the total eclipse of August 29, 1867, near Santiago (*Astron. Nachrichten*, No. 1737, Jan. 28, 1869).

β Iodopropionic acid boiled with silver oxide not in excess, yields a silver salt, convertible by double decomposition into a zinc salt, having the composition $(C^3H^5O^3)^2Zn$, and the properties of ordinary zinc lactate; but the mother-liquor after a while deposits crusts easily soluble in water and in alcohol, and having nearly the composition of the zinc salt of paralactic or sarcolactic acid. Wichelhaus regards the latter as the primary product of the transformation of β iodopropionic acid, and supposes that it is afterwards converted into ordinary lactic acid by prolonged boiling with the silver oxide; he thence infers that α chloro- and α iodo-propionic acid are analogous in constitution to ordinary lactic acid; β chloro- and iodopropionic acid to paralactic acid:

$CH^3—CHI—CO^2H$ α Iodopropionic.	$CH^2I—CH^2—CO^2H$ β Iodopropionic.
$CH^3—CH(OH)—CO^2H$ Lactic.	$CH^2(OH)—CH^2—CO^2H$ Paralactic.

Wislicenus (*Zeitschr. f. Chem.* [2] iv. 683) also finds that β iodopropionic acid boiled with recently precipitated silver oxide, yields lactic acid, and is of opinion that the acid $C^{12}H^{22}O^{11}$, called *hydracrylic acid*, which Beilstein obtained from β iodopropionic acid by the same process, was in all probability nothing but lactic acid.

Socoloff, on the other hand (*ibid.* v. 423), has obtained by similar means an acid, $C^3H^6O^3$, some of the salts of which differ in character from those of either of the known lactic acids, and from those of the isomeric methyl-glycollic acid. This acid he designates as *glyceraldehydic acid*, regarding it as the aldehyde of glyceric acid. Beilstein's hydracrylic acid he regards as an anhydride of this acid. (See LACTIC ACID, p. 770.)

β Iodopropionic acid heated with excess of *metallic silver* is converted into adipic acid, $C^{10}H^{10}O^4$ (Wislicenus, *ibid.* 680):

$$2(CH^2I—CH^2—CO^2H) + Ag^2 = 2AgI + [CO^2H—(CH^2)^4—CO^2H].$$

Phenyl-propionic Acid. $C^9H^{10}O^2 = C^6H^5(C^3H^5O^2)$.—Syn. with HYDROCINNAMIC ACID. See CINNAMIC ACID (p. 468). Under the same head are also described the chlorine, bromine, and iodine derivatives of phenyl-propionic acid, also of oxyphenyl-propionic or phenyl lactic acid, $C^9H^{10}O^3$.

Nitrophenyl-propionic acid, $C^9H^9(NO^2)O^2 = C^6H^4\begin{cases}NO^2\\C^3H^5O^2\end{cases}$, is formed by treating hydrocinnamic acid with fuming nitric acid in a cooled vessel; when purified by separation from its sodium salt and recrystallisation from hot water, it forms feathery groups of faintly yellow crystals, very slightly soluble in cold, more easily in warm water, moderately soluble in alcohol and ether. It softens when heated, melts completely at 153°, and solidifies to a radio-crystalline mass on cooling. Its salts are for the most part easily soluble and difficult to crystallise; the lead and silver salts are yellowish precipitates. The acid oxidised with chromic acid mixture is converted into paranitrobenzoic acid: hence it belongs to the para series.

Amidophenylpropionic acid, $C^9H^9(NH^2)O^2 = C^6H^4\begin{cases}NH^2\\C^3H^5O^2\end{cases}$, is formed, together with hydrocarbostyrol (p. 715), by treating the nitro-acid with tin and hydrochloric acid, and remains in the mother-liquor after the hydrocarbostyrol has been separated. It crystallises in groups of quadratic prisms, melting at 131° and decomposing at higher temperatures. It unites both with bases and with acids; but the salts which it forms with bases are unstable and difficult to crystallise. Its combinations with acids, on the other hand, crystallise well: the *hydrochloride*, $C^9H^{11}NO^2.HCl$, in groups of four-sided prisms; the *sulphate*, $2C^9H^{11}NO^2.H^2SO^4$, from water, in large nodular groups; from alcohol it is precipitated by ether in silky needles; the *nitrate* separates from solution in warm dilute nitric acid in fine crystals.

Chloride of Diazophenylpropionic acid, $C^9H^7N^2O^2Cl = C^6H^4\begin{cases}N{=}NCl\\C^3H^5O^2\end{cases}$, is produced by passing nitrous acid vapour to saturation into a solution of *dry* hydrochloride of amidophenylpropionic acid in absolute alcohol, and crystallises in four-sided needles which detonate when heated. Their aqueous solution when warmed gives off large bright line, and widened out on both sides two or three times in the very small spots: becoming bright near a spot, and expanding over it on both sides; very many times widened out near a spot, sometimes considerably, on the less refrangible side; and finally extended as a bright line without any thickening over a small spot (Lockyer).

Measuring the deviation of the line thus noticed, by means of Ångström's map in ten-millionths of a millimetre, Lockyer has frequently noticed a deviation corresponding to a velocity of 20 miles per second. On one occasion the F line was seen to be *triple*, showing that the hydrogen on the sun's surface under observation was moving with very different velocities, the extreme alterations of wave-length corresponding to the enormous velocity of 120 miles per second—if the explanation thus given be in reality the correct one.

The spectroscopic changes which are thus seen are sometimes connected with telescopic ones. Thus, on April 21, at 7.30 A.M., a tremendous action was observed in a prominence, for the lines C, D, and F were magnificently bright in the ordinary spectrum itself over the spot-spectrum. The injection into the chromosphere surpassed everything previously seen, as there was a magnesium cloud quite separated from the limb, and high up in the prominence itself. The photographic picture of the solar disc, made at Kew on the same day at 10.55 A.M., showed that an area of great disturbance surrounded the spot, and a subsequent photograph, at 4.1 P.M., showed the limb to be actually broken in that particular place; the photosphere seemed to have been actually torn away behind the spot, exactly when the spectroscope had afforded to Lockyer evidence of a cyclone.

F. Zöllner (*Pogg. Ann.* cxxvii. p. 624) has also noted some very interesting facts respecting the enormously rapid motion of the protuberances, and accompanying the paper are a series of drawings showing the changes which the red flames undergo.

For the description of the phenomena observed in a total eclipse, especially on the nature of the corona, works on spectroscopic astronomy may be consulted. It may here be stated that the spectrum of the corona contains one bright green line identical in refrangibility with an iron line marked 1474 on Kirchhoff's scale.

Further Spectroscopic Researches on the Stars, Nebulæ, and Comets by W. Huggins.—Dr. Huggins (*Phil. Trans.* 1868, p. 529), by employing a much more powerful train of prisms than he had previously used, endeavoured to ascertain whether any deviation in the position of the nebular or stellar lines was visible, which deviation, if it existed, would, according to Doppler's theory, indicate motion with respect to these bodies and the earth. The first object examined was the great nebula in Orion: the brightest line of the nitrogen spectrum (which can be so reduced in luminosity as to leave only this line visible) was found to be coincident with the nebular line within the limits of observational error, so that Huggins concludes that the nebula is not receding from the earth with a velocity greater than 10 miles per second, and that it is not approaching the earth with a velocity greater than 25 miles per second. The position of the F line in the Sirius-spectrum was next carefully examined; this was found to be broader than the corresponding hydrogen line, and also broader than the dark solar line F. The position of the Sirius F line is slightly less refrangible than the hydrogen line, and Huggins believes that this may be received as representing a motion of recession between Sirius and the earth, amounting to 41·4 miles per second; or, subtracting the earth's proper motion, we have a motion of recession of 29·4 miles per second, which we appear entitled to attribute to Sirius.

The spectrum of Comet II., 1868, has also been examined by Dr. Huggins; this consisted of 3 bands, identical in position with the bands obtained by passing the spark throught olefiant gas, and hence it appears that incandescent carbon, either in the free or possibly in the combined state, exists in cometary matter. The spectrum of Comet I., 1871, has also been examined by Huggins, who concludes that it possesses a constitution similar to those of 1868.

Variable Stars.—The spectrum of γ Cassiopeiæ appears to be in some respects at least analogous to that of T Coronæ (v. 395). In addition to the bright line near the boundary of the green and blue observed by Padre Secchi, there is a line of equal brilliancy in the red and dark absorption lines. Huggins has shown that these bright lines are coincident with the lines C and F, showing the presence in this star of incandescent hydrogen. MM. Wolf and Rayet have also observed bright lines in several other small stars. Padre Secchi (*Astronomische Nachrichten*, Jan. 28, 1869) finds it possible to class stars into four groups, each characterised by a special form of spectrum. Group 1 contains the white stars Sirius, α Lyræ, Vega, &c., whose spectrum is characterised by four black lines coincident with those of hydrogen. Group 2 contains the yellow stars, having spectra intersected by numerous fine lines resembling those of our sun; in this group Secchi reckons Pollux, Capella,

γ Aquilæ, and our Sun. The 3rd group contains the red and orange stars, α Orionis, α Herculis, β Pegasi, &c., the spectra of which are divided into 8 or 10 parallel columnar clusters of dark and bright bands increasing in intensity towards the red. Group 4 is made up of the small red stars, whose spectra are distinguished by a succession of three bright zones, increasing in intensity towards the violet. Out of 316 stars examined, Secchi found that 164 belonged to the first group, and 140 to the second, whilst the few remaining constituted the third and fourth classes.

Spectra of the Aurora Borealis and of the Zodiacal Light.—Ångström (*Spectre normal du Soleil*) and O. Struve have observed the spectrum of the aurora. This light is found to be monochromatic; one brilliant band situated to the left of the green calcium lines only is seen. Ångström found the wave-length of this ray to be 5567 (ten millionths of a millimetre). The same observer also succeeded in observing the same bright band in the spectrum of the zodiacal light, and during a star-light night, when the sky appeared almost phosphorescent, traces of this band were visible from all parts of the heavens. This bright band does not coincide with the known rays of any simple or compound body yet examined.

Recent General Literature on the Subject.—Roscoe's *Lectures on Spectrum Analysis, with Lithographic Copies of the Maps of Kirchhoff, Ångström, and Huggins* (Macmillan), 2nd edition, 1870. Schellen, *Die Spectralanalyse*, Braunschweig (Westermann), 1870; English translation, 1871. Secchi, *Le Soleil*, Paris, 1870. Proctor, *The Sun* (Longmans), 1871. Delaunay, *Analyse spectrale, Annuaire du Bureau des Longitudes*, 1869. R. P. A. Secchi, *Sugli Spettri dei Corpi Celesti*, Memorie, Roma, 1868; *Spettri delle Stelle fisse*, Mem. I. and II. Ångström, *Recherches sur le Spectre normal du Soleil*, Upsala, 1868. A full list of memoirs on spectrum analysis is given at the end of Roscoe's *Lectures*. H. E. R.

SPHERITE. An hydrated aluminium phosphate occurring on hæmatite at Zajecon, north of St. Benigna, in isolated or botyroïdally grouped spherules of light grey colour, passing more or less into red and blue. Sp. gr. 2·53. Hardness 4. Its analysis gave:

P^2O^5	Al^2O^3	H^2O	MgO	CaO	SiO^2		
28·58	42·36	24·03	2·61	1·41	0·87	=	99·86

leading (after deduction of the lime and magnesia as phosphates) to the formula $5Al^2O^3.2P^2O^5 + 16H^2O$ (Zepharovich, *Jahresb.* 1867, p. 1001).

SPHEROSIDERITE. This mineral, occurring in the Anamesite district of the lower Mainthal, near Steinheim, mostly in spherical or botyroïdal masses, was found by Hornstein (*Jahresb.* 1867, p. 1006) to contain:

FeO	CaO	MgO	MnO	CO^2		
61·25	0·02	0·61	trace	38·12	=	100.

STAFFELITE. A calcic phosphate mixed with carbonate, fluoride, &c., occurring as an incrustation on phosphorite at Staffel, also in the Jura limestone at Erzberg near Amberg (Stein, *Jahresb.* 1866, p. 947; Petersen, *ibid.* 1867, p. 1002).

STARCH. Observations on the occurrence and behaviour of starch, or an amylaceous substance, in the lacteal vessels of various *Apocyanaceæ*, have been made by Trécul (*Compt. rend.* lxi. 156); on the starch-granules in *Floridaceæ* and *Corallinaceæ* by van Tieghem (*ibid.* 512). C. Dareste (*ibid.* lxiii. 1142) found in egg-yolk a considerable number of microscopic granules, which were coloured by iodine, and were very much like starch in form and structure.

Flückiger (*Zeitschr. anal. Chem.* v. 302) has determined the sp. gr. of starch from arrowroot and potatoes by means of petroleum. These results are:

	Arrowroot.		Potato-starch.	
	Air-dried	Dried at 100°	Air-dried	Dried at 100°
Sp. gr. at 17°–18° . .	1·5045	1·5684	1·5029	1·6330

According to Payen (*Compt. rend.* lxi. 512; *Jahresb.* 1865, p. 596), starch immersed in a saturated solution of potassium bromide or iodide swells up to a pasty mass of 25 to 30 times its original bulk, which dissolves in water, leaving a very small quantity of membrane; iodine-water added to the solution throws down iodide of starch in flocks. As cellulose is not attacked by bromide or iodide of potassium, Payen regards these salts as well adapted for the detection of starch in vegetable tissues. Iodide of starch, precipitated from its aqueous solution by potassium chloride, and then decolorised by a small quantity of ammonia, loses in the course of an hour the power of recovering its colour on addition of acetic acid; when precipitated by sodium chloride it retains this power longer. On the decoloration of iodide of starch, see also Magnes-Lahens, *Bull. Soc. Chim.* [2] vi. 79; *Jahresb.* 1866, p. 664.

Conversion of Starch into Glucose and Dextrin.—It is generally supposed that in the action of acids or of diastase upon starch, the starch is first converted into dextrin by a mere alteration of physical structure, and that the dextrin is then converted into glucose by taking up the elements of water, this second stage of the process occupying a much longer time than the first; but from the experiments of Musculus (*Compt. rend.* l. 785; liv. 194; *Ann. Ch. Phys.* [3] lx. 208) it appears that both dextrin and glucose are produced at the very commencement of the reaction, and always in the proportion of 1 mol. glucose to 2 mol. dextrin, whence it may be inferred that the molecule of starch contains $C^{18}H^{30}O^{15}$, and that it is resolved into glucose and dextrin by taking up 1 mol. water:

$$\underset{\text{Starch.}}{C^{18}H^{30}O^{15}} + H^2O = \underset{\text{Glucose.}}{C^6H^{12}O^6} + \underset{\text{Dextrin.}}{2C^6H^{10}O^5}$$

When the conversion is effected by a dilute acid, the dextrin is, after several hours' boiling, completely converted into glucose; but when diastase is used as the converting agent, the production of glucose goes on only so long as there is any unaltered starch still present, the dextrin undergoing no further alteration. These views have been contested by Payen (*Compt. rend.* liii. 1217; *Ann. Ch. Phys.* [4] iv. 286; *Jahresb.* 1861, p. 717; 1865, p. 597), who finds that diastase really possesses the power of converting dextrin into sugar, but that the conversion ceases as soon as a certain quantity of sugar has been produced; if however the sugar be removed as fast as it is formed, as in alcoholic fermentation, the transformation of the dextrin into sugar recommences, and goes on nearly to completion. Under favourable circumstances of the action of diastase on dextrin, a product may be obtained containing more than 50 per cent. of sugar. Musculus, on the other hand (*Ann. Ch. Phys.* [4] vi. 177), adheres to his view of the unalterability of pure dextrin by diastase, and endeavours to show that the formation of sugar observed by Payen was due to the presence of amylaceous substance in the dextrin submitted to experiment. According to O. Philipp (*Bull. Soc. Chim.* [2] viii. 363), dextrin and glucose are not formed in constant proportions in the action of dilute sulphuric acid upon starch, as asserted by Musculus, but the proportion of glucose increases under otherwise equal circumstances with the quantity of acid employed. This however is quite in accordance with the known fact —not denied by Musculus—that dextrin is gradually converted into glucose by the action of dilute acids.

STEAROLIC ACID. $C^{18}H^{32}O^2$ (Overbeck, *J. pr. Chem.* xcvii. 159).—Produced by heating monobromoleic acid or oleic dibromide to 100° with at least 2 mol. potassium hydrate in alcoholic solution, and may be separated from the dilute decanted solution by hydrochloric acid. It crystallises from alcohol in silky needles or long prisms, melts at 48°, and distils at 260°, for the most part undecomposed. The salts are mostly well crystallised and become strongly electric by friction. The barium salt is anhydrous; the calcium salt contains $(C^{18}H^{31}O^2)^2Ca + H^2O$; the silver salt, $C^{18}H^{31}O^2Ag$, is a crystalline precipitate.

Stearolic acid is not affected by nascent hydrogen. In contact with bromine it forms *stearolic dibromide* (or dibromoleic acid), $C^{18}H^{32}Br^2O^2$, which when pure is a nearly colourless heavy oil, soluble in alcohol and ether, but insoluble in water. *Stearolic tetrabromide* (or tetrabromostearic acid), $C^{18}H^{32}Br^4O^2$, produced by the action of bromine in excess on stearolic acid in sunshine, crystallises in large white laminæ, which melt at about 70°, and soften even when rubbed. Both these bromine-compounds are decomposed by prolonged heating with alcoholic potash, forming stearolic acid, and a liquid acid not yet examined.

Stearolic acid fused with excess of potash at a rather high temperature is converted into myristic acid, $C^{14}H^{28}O^2$; at a lower temperature, if the action be arrested as soon as gas begins to escape, it yields an acid, $C^{16}H^{30}O^2$, isomeric or identical with hypogæic acid (Marasse, *Zeitschr. f. Chem.* [2] v. 571).

STEAROXYLIC ACID, $C^{18}H^{32}O^4$, is formed, together with azelaic acid and azelaic aldehyde, by dropping fuming nitric acid into cooled stearolic acid, and remains in the residue left on treating the semifluid mass with water. It crystallises from alcohol in faintly yellowish oblique rhombic tables, slightly soluble in cold alcohol, easily in hot alcohol and in ether, melting at 86°, and scarcely decomposing at 200°. It is monobasic and does not unite directly with bromine. Its *silver salt*, $C^{18}H^{31}O^4Ag$, is precipitated on mixing the acid with silver nitrate in hot alcoholic solution, as a white crystalline powder which does not decompose at 100°. The *barium salt*, by converting the latter, first into ethyl cyanide or propionitrile, $CH^3—CH^2—CN$, then into propylamine, $CH^3—CH^2—CH^2—NH^2$, by the action of nascent hydrogen, and the latter into propyl alcohol by heating the aqueous solution of its nitrite (p. 63). This series of actions might rather be expected to yield normal propyl alcohol, $CH^3—CH^2—CH^2OH$; but the greater part of the alcoholic liquid obtained was found to boil at 83°–85°, and to yield acetone by oxidation: it was therefore isopropyl alcohol. A smaller portion boiled at 93°–96°, and appeared to be the same alcohol mixed with a small quantity of a foreign substance. The change of the propyl radicle from normal propyl, $CH^2CH^2CH^3$, into isopropyl, $CH(CH^3)^2$, probably takes place in the conversion of the propionitrile into propylamine. The formation of the alcohol is accompanied by that of a nitrogenous substance, $C^6H^{14}N^2O$, boiling between 200° and 205°, having a sp. gr. of 0·924 at 14°, and slightly soluble in water (Siersch, *Ann. Ch. Pharm.* cxliv. 137; see also Linnemann, *ibid.* cl. 370).—γ. Dichlorhydrin, $CH^2Cl—CHOH—CH^2Cl$, dissolved in ether free from alcohol, but not anhydrous, is converted by sodium-amalgam into isopropyl alcohol, mixed with products of higher boiling point (Buff, *Zeitschr. f. Chem.* [2] iv. 124).—δ. Glycolic iodhydrin, $C^2H^4I(OH)$, treated with zinc-methyl, yields the compound $\left.\begin{matrix}C^3H^7\\(CH^3Zn)'\end{matrix}\right\}O$, and this, when heated with water under pressure, is converted into isopropyl alcohol (Butlerow a. Ossokin, p. 64). Yssel de Schepper a. Tak (*ibid.* iv. 520) have obtained isopropyl alcohol from the portion of grain fusel-oil boiling at 93°–98°, by boiling it with potash in a flask with upright condenser and distillate. The distillate dehydrated with sodium carbonate yielded a propyl alcohol boiling at 83°–84°, and convertible into an iodide boiling at 72°–91°.

Isopropyl alcohol subjected to a series of processes exactly similar to that by which it is formed from ethyl alcohol, yields an alcohol, $C^4H^{10}O$, probably consisting of isobutyl alcohol (Siersch, *Ann. Ch. Pharm.* cxlviii. 261; *Jahresb.* 1868, p. 436).

The *haloïd isopropyl ethers*, formed by treating the alcohol with the corresponding hydracids, exhibit the following properties:

	Boiling point.	Sp. gr.
Isopropyl chloride . . .	36° to 38° at 741 mm.	0·874 at 10°
„ bromide . . .	60 „ 63° „ 739 „	1·320 „ 13°
„ iodide . . .	89 „ 90° „ 735 „	1·70 „ 15°

The action of bromine on isopropyl alcohol gives rise (inasmuch as acetone and hydrobromic acid are formed by abstraction of water) to isopropyl bromide, propylene bromide, and substitution-products of acetone, from which, by the action of potash, bromoform may be produced. Isopropyl chloride is but little attacked by chlorine or bromine. Isopropyl iodide is converted, by the action of chlorine or of hydrochloric acid and potassium chlorate, into a product boiling between 90° and 170°, from which, by fractional distillation, trichlorhydrin, $C^3H^5Cl^3$ (b. p. 154°–159°; sp. gr. 1·417 at 15°), may be separated. Bromine converts isopropyl iodide into the bromide. When equal volumes of bromine and isopropyl bromide are heated with water to 140°–150°, monobromisopropyl bromide, $C^3H^6Br^2$, is formed, together with further substitution-products. This compound is identical with propylene bromide, boils at 140°–143°, and has a sp. gr. of 1·954 at 150°. By silver acetate in presence of glacial acetic acid it is converted into propylene diacetate (b. p. 180°–185°), and by alcoholic potash into monobromopylene, C^3H^5Br (b. p. 56°–58°; sp. gr. 1·40 at 13°). This last compound unites with bromine, forming the compound $C^3H^5Br.Br^2$ (b. p. 194°–196°; sp. gr. 2·390 at 10°), identical with that previously obtained by Wurtz (*Jahresb.* 1857, p. 462) and by Cahours (*ibid.* 1850, p. 496). Heated with silver acetate and glacial acetic acid to 110°–120°, it is converted, as shown by the equation,

$$C^3H^5Br^3 + C^2H^3AgO = C^3H^4Br^2 + C^2H^4O^2 + AgBr,$$

into *dibromopropylene*, $C^3H^4Br^2$ (b. p. 127°–131°; sp. gr. 1·98 at 15°), which is identical with allylene bromide, inasmuch as, when treated with sodium, it gives off a gas exhibiting all the properties of allylene.

When isopropyl bromide and water are heated with 2 mol. bromine to 110°–120°, a colourless liquid is formed, which on distillation at 180° yields isopropyl bromide and propylene bromide, whilst the residue contains a mixture of more highly brominated substitution-products. After prolonged standing in the cold, it deposits a large quantity of crystallised *tribromisopropyl bromide*, $C^3H^4Br^3.Br$, while the expressed oily mother-liquor contains, in the portions boiling between 180° and 200°, *dibromisopropyl bromide*, $C^3H^5Br^2.Br$. This compound is converted by silver oxide into an easily soluble silver salt, an oily liquid insoluble in water, boiling above 150°, depositing radiate groups of needles. The *mercury-compound* $C^{21}H^{22}N^2O^2.HI.HgI^2$ is produced by agitating a hot alcoholic solution of the tri-iodide with mercury. It is insoluble in water, very slightly soluble in hot alcohol, from which it crystallises in light yellow shining tables. Similar crystallised double salts are obtained by heating the solution of strychnine tri-iodide with zinc and magnesium. *Methyl-strychnine tri-iodide*, $C^{21}H^{22}N^2O^2.CH^3.I^3$, crystallises from an alcoholic solution of 1 mol. methyl-strychnine hydriodide and 1 mol. iodine, in long brown-yellow needles, which in polarised light appear pale yellow or purple-red. *Ethyl-strychnine tri-iodide*, $C^{21}H^{22}N^2O^2.C^2H^5.I^3$, crystallises from alcohol in long four-sided needles exhibiting similar appearances in polarised light. The same is true of the *amyl-compound*, $C^{21}H^{22}N^2O^2.C^5H^{11}.I^3$. From a solution of the latter in tincture of iodine, the *pentiodide*, $C^{21}H^{22}N^2O^2.C^5H^{11}.I^5$, crystallises in almost black needles exhibiting under the microscope by reflected light the lustre of polished steel. In polarised light they appear opaque when their axis is parallel to the plane of polarisation, dark purple-violet in the perpendicular position (Jörgensen, *Ann. Ch. Phys.* [4] xi. 115; *Jahresb.* 1867, p. 525).

A compound of strychnine with *hydrogen persulphide*, $C^{21}H^{22}N^2O^2.H^2S^3$, is obtained by mixing a cold-saturated solution of strychnine in strong alcohol with an alcoholic solution of ammonium sulphide containing free sulphur, and separates gradually in orange-red needles, which, after decantation of the mother-liquor, may be washed with cold alcohol. They are perfectly insoluble in water, alcohol, ether, and carbon bisulphide. Strong sulphuric acid decolorises them, and on adding a little water, hydrogen persulphide separates in oily drops, while the solution contains strychnine sulphate (Hofmann, *Deutsch. chem. Gesellsch. Berlin.* 1868, p. 81; *Zeitschr. f. Ch.* [2] iv. 502). See also H. How (*Chem. News*, xviii. 232).

Methyl-strychnine is much less poisonous than strychnine. The nitrate given in doses of 0·05 to 0·2 grm. does not act poisonously on dogs or rabbits when taken internally; by subcutaneous injection it produces symptoms of paralysis similar to those produced by curara (Schroff, *Jahresb.* 1866, p. 474). The hydriodide of the same base produces, not tetanus, but paralysis, like curara. 20 grains administered subcutaneously killed a rabbit; 30 grains introduced into the stomach produced no effect. The sulphate was much more active, but did not cause death by subcutaneous injection in doses of less than a grain (Crum Brown and Fraser, *Edinb. Phil. Trans.* vol. xxv.; *Jahresb.* 1868, p. 756).

STYPHNIC ACID. Syn. with OXYPICRIC ACID (p. 892).

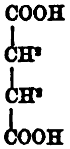
STYRROL. Syn. with CINNAMENE (p. 465).

SUBERIC ALDEHYDE, $C^8H^{14}O^3$, is formed, together with suberic acid and palmitoxylic acid, by the action of fuming nitric acid on palmitolic acid (p. 895):

$$\underset{\text{Palmitolic acid.}}{2C^{16}H^{28}O^2} + O^7 = \underset{\text{Palmitoxylic acid.}}{C^{16}H^{28}O^4} + \underset{\text{Suberic acid.}}{C^8H^{14}O^4} + \underset{\text{Suberic acid.}}{C^8H^{14}O^3}$$

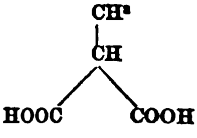
The suberic acid is extracted from the product by boiling water; the residue is dissolved in hot alcohol; and the lower dark-coloured oily layer which separates from the filtrate on cooling, and consists chiefly of suberic aldehyde, is separated from the supernatant solution of palmitoxylic acid, gently warmed to expel the alcohol, then distilled in a stream of aqueous vapour. The oil which floats on the watery distillate is dissolved in alcohol, and the solution is evaporated in a vacuum, whereupon the suberic aldehyde remains as an oil having a faint odour. It boils with partial decomposition at 202°; leaves a difficultly combustible cinder when quickly heated on platinum foil; and is converted by oxidising agents (bromine and water) into a crystalline acid having the appearance and melting point of suberic acid (Schröder, *Jahresb.* 1866, p. 327).

SUCCINIC ACID. $C^4H^6O^4$.—This acid exhibits two modifications corresponding to those of chloropropionic and of lactic acid (p. 969); viz.,



$$\begin{array}{l}COOH\\ |\\ CH^2\\ |\\ CH^2\\ |\\ COOH\end{array}$$

Ethylene-dicarbonic or
Ordinary Succinic acid

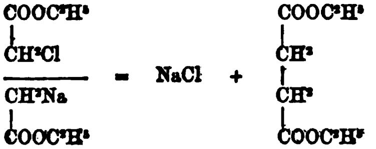


Ethylidene-dicarbonic or
Isosuccinic acid

the former corresponding to *β*-chloropropionic and paralactic acid, the latter to *α*-chloropropionic and ordinary lactic acid.

Ordinary succinic acid is formed by heating phenaconic acid to 150° in a sealed tube with hydriodic acid of 50 p. c.; slowly also by the action of dilute hydriodic acid or of sodium-amalgam: $2C^6H^6O^6 + H^6 = 3C^4H^6O^4$.

The ethylic ether of ordinary succinic acid is produced by the action of ethyl monochloracetate on the product of the action of sodium on acetic ether (ethylic sodacetate, $CH^2Na.CO^2C^2H^5$, or acetate of ethylene-sodium, $NaC^2H^4.C^2H^3O^2$):



$$\frac{\begin{array}{l}COOC^2H^5\\ \vert\\ CH^2Cl\end{array}}{\begin{array}{l}CH^2Na\\ \vert\\ COOC^2H^5\end{array}} = NaCl + \begin{array}{l}COOC^2H^5\\ \vert\\ CH^2\\ \vert\\ CH^2\\ \vert\\ COOC^2H^5\end{array}$$

(Noeldecke, *Ann. Ch. Pharm.* cxlix. 224).

Isosuccinic or *α-succinic acid* is prepared from *α*-chloropropionic acid by distilling the ethylic ether of the latter with potassium cyanide, whereby it is converted into *α*-cyanopropionic ether, $CH^3—CHCy—COOC^2H^5$, and boiling this ether with potash; *β*-succinic or ordinary succinic acid is obtained in like manner from *β*-chloropropionic acid (H. Müller, *Ann. Ch. Pharm.* cxxxi. 108;—Wichelhaus, *Zeitschr. f. Chem.* [2] iii. 247). Ordinary succinic acid is also produced by heating either ethylic chloride (v. 454) or ethylidene chloride with potassium cyanide to 160°–180°; and boiling the product with potash; in the latter case it is probable that the ethylidene is converted into ethylene during the action of the potassium cyanide on the chloride (Maxwell Simpson, *Compt. rend.* lxv. 351; see also Mühlhäuser, *Zeitschr. f. Chem.* [2] iii. 593; v. Richter, *ibid.* iv. 451). Other modes of formation of ordinary succinic acid are: *a.* By oxidation of benzoic acid with dilute sulphuric acid and lead dioxide, and in the animal organism (Meissner a. Shepard, *Jahresb.* 1866, p. 397).—*b.* By oxidation of paraffin with strong nitric acid (Gill a. Meusel, p. 708).—*c.* By the action of powerful reducing agents, *e.g.* saturated hydriodic acid at 150°–180°, or tin and hydrochloric acid, on trichlorophenomalic acid, $C^6H^7Cl^3O^5$ (p. 917), this acid being first converted into phenomalic acid, $C^6H^{10}O^5$, and the latter resolved into succinic acid, and a body having the composition of acetic aldehyde: $C^6H^{10}O^5 = C^4H^6O^4 + C^2H^4O$ (Carius).

Isosuccinic acid melts at 130°, and dissolves in 5·4 pts. of cold water, whereas ordinary succinic acid melts at 170°–180°, and requires more than 20 pts. of cold water to dissolve it (Wichelhaus). According to Carius (*Jahresb.* 1866, p. 564), 100 pts. of water dissolve 3·52 pts. of ordinary succinic acid at 15°; 5·19 pts. at 17°; 6·15 pts. at 18°.* Isosuccinic acid in the form of sodium salt does not form a precipitate with ferric chloride (Wichelhaus), whereas succinic acid gives a red-brown precipitate (v. 455).

Isosuccinic acid heated to 150° does not yield an anhydride, like the ordinary acid, but is completely resolved into carbon dioxide and propionic acid: $C^4H^6O^4 = CO^2 + C^3H^6O^2$. Heated with bromine and water, it is converted much more easily than ordinary succinic acid into a monobrominated acid which, when treated with ammonia, appears to yield aspartic acid.

Isosuccinates.—A solution of the acid neutralised with an alkali is not precipitated by barium or calcium chloride. The free acid forms with lead acetate and silver nitrate, curdy precipitates which dissolve when heated. The *potassium salt* forms a mass of needle-shaped crystals. The *barium salt*, $C^4H^4O^4Ba + 2H^2O$, the *calcium salt*, $C^4H^4Ca + H^2O$, and the *zinc salt*, $C^4H^4O^4Zn + 3H^2O$, produced by boiling the acid with the respective carbonates, are obtained by evaporation as indistinctly crystalline masses, which give off their water with decomposition when heated, the barium and calcium salts at 200°, the zinc salt at 115° (V. v. Richter, *Zeitschr. f. Chem.* [2] iv. 452).

A solution containing 5 p. c. succinic acid and 1 p. c. uranic succinate turns green when exposed to sunshine, and gradually gives off carbon dioxide, leaving propionic acid in solution (Seekamp, *Ann. Ch. Pharm.* cxxxiii. 253).

Aqueous succinic acid slowly reduces *potassium permanganate* at the boiling heat; also in presence of sulphuric acid. Heated to 100° with a solution of the permanganate containing a considerable quantity of potash, it yields oxalic acid (Berthelot, *Bull. Soc. Chim.* [2] viii. 390).

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* The old determination by Lecanu a. Serbat (v. 454) must be regarded as erroneous.

Succinic acid heated with *hydriodic acid* is converted into butane:

$$C^4H^6O^4 + 12HI = C^4H^{10} + 4H^2O + 6I^2$$

(Berthelot, *Jahresb.* 1867, p. 345).

Isodibromosuccinic acid is formed, together with a small quantity of ordinary dibromosuccinic acid, and other products, by heating phenaconic acid in sealed tubes with excess of bromine and a small quantity of water (Carius, p. 905):

$$\underset{\text{Phenaconic acid.}}{C^6H^6O^6} + Br^6 = \underset{\text{Dibromo-succinic acid.}}{C^4H^4Br^2O^4} + CO^2 + \underset{\text{Bromoform.}}{CHBr^3} + HBr.$$

Thiosuccinic Acid. $C^4H^6O^2S^2$.—The potassium salt of this acid, $C^4H^4O^2S^2K^2$, is obtained by the action of potassium sulphydrate on succinyl-phenol (p. 1042), when dissolved in absolute alcohol. It crystallises in tufts of pointed needles, dissolves very easily in water, with fall of temperature, easily also in alcohol and ether. The solutions, especially the aqueous solution, decompose by spontaneous evaporation in contact with the air, leaving gummy residues having an alliaceous odour. The recently prepared solutions act on metallic salts, like the solutions of alkaline sulphides. They are quickly decomposed by acids, with evolution of hydrogen sulphide, and if concentrated, deposit thiosuccinic acid in oily drops which are crystallise (Weselsky, *Deut. chem. Ges. Ber.* ii. 518; *Zeitschr. f. Chem.* [2] v. 61).

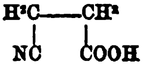
Thiosuccinyl, $C^4H^4O^2S$, is formed by decomposing an aqueous solution of potassium thiosuccinate with hydrochloric acid:

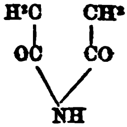
$$C^4H^4O^2S^2K^2 + 2HCl = 2KCl + SH^2 + C^4H^4O^2S.$$

The product is agitated with ether, and the ethereal extract is separated, dried with calcium chloride, and distilled. There then remains an oily residue, which when left over potash under the air-pump, solidifies to a broadly laminar crystalline mass, which remains moist for a long time. Thiosuccinyl dissolves easily in water, alcohol and ether, has a strong acid reaction, a very sweet taste, with an after-taste like that of succinic acid, and melts at 31°. Its solution gives with lead acetate a yellow precipitate quickly turning brown, black when heated, and settling as a sparkling deposit on the sides of the vessel. From solution of cupric sulphate it immediately precipitates copper sulphide. With silver nitrate it forms a white precipitate, which soon turns yellow and finally black; with ferric chloride a milky turbidity, which increases to a white precipitate, turning grey when heated, and black on addition of ammonia (Weselsky).

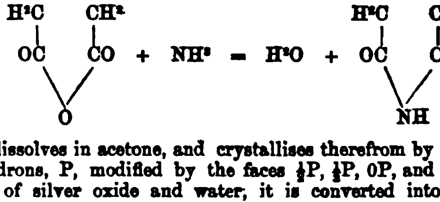
SUCCINIMIDE. $C^4H^5NO^2 = (C^4H^4O^2)''.NH$.—The melting point of this compound has hitherto been given at 210° on the authority of Fehling and of Teuchert (v. 461). Erlenmeyer (*Zeitschr. f. Chem.* [2] v. 175) has, however, shown that it melts at 125° to 126°, and this result has been confirmed by a subsequent observation of Fehling.

Succinimide is isomeric with cyano-propionic acid, the difference of constitution of the two being represented by Erlenmeyer as follows:


Cyanopropionic acid.


Succinimide.

The formation of succinimide from succinic anhydride and ammonia may then be represented by the following equation:



Succinimide dissolves in acetone, and crystallises therefrom by slow evaporation in rhombic octohedrons, P, modified by the faces $\frac{1}{2}P$, $\frac{1}{3}P$, 0P, and $\frac{1}{2}\bar{P}\infty$. Boiled with a slight excess of silver oxide and water, it is converted into silver-succinimide, $C^4H^4O^2.NAg$, which separates in crystals from the hot filtrate (Bunge, *Ann. Ch. Pharm. Suppl.* vii. 128).

Iodosuccinimide, $C^4H^4O^2.NI$, is formed by adding silver-succinimide in fine powder to a solution of iodine in alcohol or anhydrous ether, or better in pure and dry acetone, and crystallises from the filtered liquid by spontaneous evaporation in quadratic prisms, ∞P, acuminated at one end by P, and at the other by P and 2P. Axes $a : c = 1 : 0·8733$. It decomposes and turns yellow at 100°, and at 135° is converted into a brown liquid with sublimation of iodine. It dissolves very easily in acetone and in water, less easily in alcohol, still less in ether. Treated in aqueous solution with hydrogen sulphide, it yields hydriodie acid and succinimide. Boiled with silver oxide it yields silver-succinimide and silver-iodide (doubtless also iodate). It is also converted into succinimide by the action of silver nitrite on its solution in acetone (Bunge).

SUCCINYL-PHENOL, $C^4H^4O^2(OC^6H^5)^2$, is produced by heating 4 pts. succinyl chloride and 5 pts. phenol to 100° in a flask provided with a reversed condenser. The crystalline product dissolves easily in boiling absolute alcohol, and the filtered solution on cooling deposits it in nacreous laminæ. It is insoluble in water, soluble in ether, carbon bisulphide, and benzol, melts at 118°, and distils without decomposition at 330°. Bromine acts violently upon it, producing tribromosuccinylphenol, as a chalky crystalline powder, which dissolves only in a large quantity of boiling alcohol, and separates therefrom in soft white needles; it is decomposed by boiling alcoholic potash, yielding succinic acid and dibromophenol. Succinyl-phenol is not attacked by acetyl chloride even at 100° (Weselsky, *Deut. chem. Ges. Ber.* ii. 518; *Zeitschr. f. Chem.* [2] vi. 60).

SUGARS. 1. *Cane-sugar* or *Saccharose*.—W. Stein (*J. pr. Chem.* cvii. 444; *Zeitschr. f. Chem.* [2] vi. 286) has obtained from madder-root 8 p. c. of crystallised cane-sugar, and is of opinion that the total quantity of this sugar in the root amounts to 14 to 15 p. c., but that part of it is uncrystallisable (? inverted sugar).

On the optical method of estimating sugar, see E. Mulder, *Scheik. Onderz.* iii. [2] 169; *Jahresb.* 1863, p. 709;—Teirich, *Zeitschr. anal. Chem.* iii. 501;—H. Wild, *ibid.* 226, 498;—Scheibler, *ibid.* 509;—Gerlach, *Dingl. pol. J.* clxxii. 31, 286;—Scheibler, *Zeitschr. anal. Chem.* v. 240; vi. 466;—Anders, *Dingl.* clxxix. 71; *Bull. Soc. Chim.* [2] vi. 429;—Landolt, *Dingl.* clxxxvii. 251; *Zeitschr. anal. Chem.* vii. 1.

Dubrunfaut (*Dingl.* clxxxv. 231; *Jahresb.* 1867, p. 932) determines the quantity of crystallisable sugar in beet-sugar and cane-sugar by means of the polariscope, and the quantity of molasses by the alkalimetric value of the ash, this latter method being founded on the observation that molasses of similar origin yield by incineration residues containing nearly equal quantities of carbonates. A modification of this method adopted in sugar-works consists in incinerating the molasses with addition of sulphuric acid, and weighing the sulphates thus obtained.

A table for the rapid approximate determination of the proportion of sugar in a solution from its specific gravity is given by E. Anthon (*Dingl.* clxxxix. 135; *Jahresb.* 1868, p. 957).

Sp. gr.	Percentage-composition of Solution saturated at 17·5°		
	Sugar	Other Substances	Water
1·3300	66·66	0	33·34
1·3322	64·85	2·66	32·49
1·3384	63·70	5·29	31·01
1·3446	62·65	7·76	29·68
1·3509	61·42	10·13	28·45
1·3572	60·28	12·48	27·24
1·3636	59·14	14·67	26·19
1·3700	58·00	16·82	25·18
1·3764	56·85	18·87	24·28
1·3829	55·70	20·77	25·53
1·3894	54·56	22·59	22·85
1·3959	53·42	24·36	22·22
1·4025	52·28	25·98	21·74
1·4092	51·14	27·56	21·30
1·4059	50·00	29·00	21·00

Nearly all proteids when in aqueous solution or suspension are found to change in character, especially in their solubilities. These changes are very marked at a temperature of about 40°. The preparation of most of the substances is tedious, and hence the results of the examination of apparently the same substance vary exceedingly.

The compounds they form with metallic salts and other bodies are variable in composition (those with potassio-platinic cyanide no less than others) (Diakonow, *Hoppe-Seyler's Untersuch.* ii. p. 228).

They all contain nitrogen, carbon, hydrogen, oxygen (sulphur and phosphorus), in the proportions given below. That the sulphur in proteids is unoxidised is shown by their giving off sulphuretted hydrogen when treated with strong alkalis, and in various other decompositions. The phosphorus is probably present as phosphate, either mechanically attached or joined in some peculiar loose combination.

All proteid solutions are lævorotatory.

With one exception (peptones), all proteids diffuse with great difficulty.

Boiled with Millon's reagent * they all give a deposit which after a while turns red, the supernatant liquor also becoming coloured red. Heated with strong nitric acid they turn yellow, the mixture on addition of ammonia becoming a deep orange (xantho-proteic reaction).

They change the colour of the cupro-potassic test-liquid for sugar from blue to violet.

Proteids are very conveniently divided into classes as is done by Hoppe-Seyler (*Handbuch physiol. chem. Anal.*).

CLASS I. ALBUMINS.—Soluble in water.

1. **Egg-albumin.** *Preparation.*—The white of hen's egg is diluted with an equal bulk of water, well stirred, strained, treated with dilute acetic acid as long as any precipitate falls, filtered, carefully neutralised, and concentrated to the original bulk at a low temperature.

Characters.—A neutral, transparent, generally faintly yellowish fluid, turning the plane of polarisation to the left, the specific rotation being 35·5° for yellow light (sodium flame). Heated to about 70° the whole or greater part of the substance is thrown down as a flocculent or curdy precipitate. The supernatant liquid, always more alkaline than before, is generally opalescent, from the formation of alkali-albumin (see below).

By careful acidulation all proteid matter is thrown down, and a perfectly clear filtrate obtained.

The substance thus thrown down is not a mere precipitate. It differs radically in its characters from soluble albumin, is remarkable by its great insolubility, and is called *coagulated* albumin (see below.)

The exact temperature at which this coagulation by heat takes place is much affected by various circumstances, notably by the presence of neutral salines, which lower the point of coagulation.

Treated with excess of alcohol, egg-albumin is wholly precipitated from its solutions. If the alcohol be rapidly filtered off, the precipitate may be wholly or in great part redissolved in water. Within a short time, however, it is found that, under the influence of the alcohol, the precipitate passes into the coagulated state; the longer the alcohol is allowed to act, the greater is the proportion of the material coagulated.

By strong mineral acids, especially by nitric acid, egg-albumin is precipitated and coagulated.

Metallic salts, such as mercuric chloride, silver nitrate, lead acetate, give a precipitate containing variable quantities of the precipitant. The lead precipitate suspended in water, treated with sulphydric acid to remove the lead, and neutralised, gives a solution of albumin. The white of egg always contains saline matters, which are retained in the solution of albumin prepared as above. All attempts completely to remove these salines by dialysis, &c., have failed, and it is still an open question whether they in part are in some way intimately associated with the albumin, and whether their presence is not essential to its being in a state of solution.

2. **Serum-albumin.** *Preparation.*—Serum of blood is diluted with water, treated with dilute acetic acid as long as any precipitate appears, filtered, neutralised, and reduced to its original bulk at a low temperature.

Characters.—Thus prepared, serum-albumin agrees in its main features with egg-albumin. They differ in the following points:

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* *Millon's Reagent.*—Equal quantities of mercury and strong nitric acid are mixed and gently warmed till the mercury is dissolved. The solution is diluted with twice its bulk of water, and the copious precipitate allowed to settle. The clear supernatant liquid is the reagent.

The specific rotation of serum-albumin is 56° for yellow light.

Egg-albumin agitated with ether is coagulated. If the solution be dilute, the coagulum appears on standing at the junction of the two liquids. Serum-albumin is not coagulated by ether.

Egg-albumin is very readily coagulated by strong hydrochloric acid; the coagulum redissolves with very great difficulty. Serum-albumin is not so readily coagulated by the same acid; the coagulum redissolves readily.

CLASS II. GLOBULINS.—Insoluble in water, soluble in very dilute acids and alkalis, soluble in dilute (1 p. c.) solutions of sodium chloride and other neutral salts.

1. **Myosin.** *Preparation.*—Fresh muscle finely minced is rapidly washed with distilled water until the wash-water gives no signs of containing proteids or of being acid, and is then treated with a 10 or 5 p. c. solution of sodium chloride. The resulting viscid mass is strained through linen, filtered through coarse paper, and dropped little by little into a large quantity of distilled water. A large flaky precipitate is thus produced which settles on standing. The liquid is removed by decantation and filtration, the precipitate redissolved in the saline solution, filtered, and again precipitated with water.

Characters.—Insoluble in water. Readily soluble in sodium chloride solutions, of ·1 to 10 or more p. c. (also in other neutral saline solutions). From these solutions myosin is precipitated either by extreme dilution or by saturation. On adding the solid salt to a sodium chloride solution of myosin, the liquid becomes more and more viscid, and just as the point of saturation is reached, the whole of the myosin is precipitated. The precipitate may then be separated by filtration, and washed if necessary with saturated solution of the salt. The amount of salt still adhering to it is sufficient to render it capable of being dissolved when treated with distilled water.

Treated either by the method of dilution or of saturation, the myosin remains unchanged by the action of the reagents.

Exposed, however, either in solution or suspension for any length of time, especially at a temperature of 20°-40°, myosin changes in solubility, becoming less and less soluble in dilute neutral saline solutions. The same change may be brought about instantaneously by dilute acids or alkalis. Myosin is exceedingly soluble in dilute acids. The solutions are uncoagulated by boiling, indeed apparently unchanged. On neutralisation the whole of the proteid is thrown down; the acid solution is also precipitated by the addition of neutral salines. The precipitate, however, is no longer myosin; it is no longer soluble in dilute neutral saline solution; it has passed into Class III. In like manner myosin is extremely soluble in dilute alkalis; the whole of the dissolved proteid may be precipitated on neutralisation, but the precipitate is no longer soluble in dilute neutral salines; it too belongs to Class III.

Suspended in water and heated to 70°, myosin enters into the insoluble or coagulated condition. The neutral saline solutions of myosin are coagulated by heat.

Just as fibrin (see below) does not exist as such in living blood, so myosin does not exist as such in living muscle. It makes its appearance *pari passu* with the condition of muscle known as *rigor mortis* (of the mechanical phenomena of which it is most probably the cause), by a process similar to the coagulation of blood. If living, still irritable muscle, freed as much as possible from blood and lymph (the muscle of frog is most convenient for the purpose), be frozen, minced, mixed with snow containing 1 per cent. of sodium chloride, and powdered, at a temperature below freezing point, the mixture may with great care be filtered when melting. The filtrate speedily (at the temperature of the body almost immediately) sets into a gelatinous mass, which afterwards separates by contraction into a clot and serum. The clot, however, has the characters, not of fibrin, but of myosin.

2. **Globulin.** (*Paraglobulin.*) *Preparation.*—When fresh blood-serum is diluted tenfold with water, and a brisk stream of carbonic acid passed through it, a fine granular precipitate is formed, which may be separated by decantation and filtration, and washed with water.

It may also be prepared by saturating blood-serum with sodium chloride (or magnesium sulphate, &c.), as in the case of myosin. A certain amount of the salt will cling to the precipitate.

Characters.—Globulin is exceedingly soluble in dilute saline solutions (from which it may be precipitated unchanged by carbonic acid gas or *exceedingly* dilute acids). Insoluble in water, it is dissolved however when the water is saturated with oxygen.

precipitate with hydrogen sulphide. By boiling with dilute acids it is resolved into rhamnetin and glucose (Schützenberger).

3. **Laevulose. Inverted Sugar.** This kind of sugar exists, together with saccharose, in the sugar-cane, especially in the upper parts of the stem which are still enveloped by the green leaves, and thereby protected from light; in these it sometimes amounts to ⅓ of the quantity of saccharose. As the leaves dry up, and the upper part of the stem becomes exposed to light, the uncrystallisable sugar gradually becomes converted into crystallisable saccharose; in the lower part of the stem the proportion of uncrystallisable to crystallisable sugar does not exceed $\frac{1}{75}$ to $\frac{1}{50}$. It is probable therefore that the crystallisable sugar of the cane is only a secondary product formed by the action of light on the fruit-sugar originally existing in the stem (Icery, *Ann. Ch. Phys.* [4] v. 350; *Jahresb.* 1865, p. 819).

Gräger (*N. Jahrb. Pharm.* xxix. 294) has made a series of experiments on the mode of conversion of cane-sugar into grape-sugar (more correctly inverted sugar) by dilute tartaric acid in presence of alcohol. In solutions containing from 6·8 to 10 pts. of tartaric acid per thousand, the transformation takes place very slowly at ordinary, more quickly at higher temperatures, *e.g.* at 45°. In an alcoholic mixture of 14 pts. alcohol, 10 pts. cane-sugar, 1 pt. tartaric acid, and 79 pts. water, 93 p. c. of the sugar was transformed into inverted sugar in 14 weeks (at about 18°). In wine the transformation takes place much more quickly; nevertheless wine loses the power of rapidly converting cane-sugar into inverted sugar when heated to 60°–70°.

On the nature of inverted sugar, see Maumené a. Dubrunfaut (*Compt. rend.* lxi. 1008, 1151, 1242, 1366; *Zeitschr. f. Chem.* [2] vi. 149).

4. **Galactose.** Pasteur, by treating milk-sugar with dilute acids, obtained a sugar thus designated, having the composition $C^6H^{12}O^6$ (iii. 1023). According to Fudakowski (*Zeitschr. f. Chem.* [2] iii. 32; *Bull. Soc. Chim.* [2] vi. 238), milk-sugar boiled with very dilute sulphuric acid yields two kinds of sugar, one of which, *a*, crystallises from the syrup freed from the acid and from lime, on addition of alcohol, while the other, *b*, separates after some time from the mother-liquor. The sugar *a* forms, after recrystallisation, small rectangular prisms with two end-faces; the sugar *b* crystallises in the six-sided tables observed by Pasteur. Both are fermentable, dextrogyrate, moderately soluble in water, but differ by their solubility in alcohol, the tabular sugar *b* being much the more soluble of the two; it appears also to have a sweeter taste and to be more easily fermentable. The specific rotatory powers of the solutions after warming or long standing are as follows:

	C	D	E
For the sugar *a* . . .	73·66°	92·83°	112·02°
For the sugar *b* . . .	50·37°	62·83°	83·03°

Both these sugars, like grape-sugar or milk-sugar, exhibit, immediately after solution in cold water, a greater rotatory power than after standing or warming.

5. **Pectin-sugar** or **Pectinose.** $C^6H^{12}O^6$.—See PECTOUS SUBSTANCES (p. 903).

6. **Sugar** from **Carminic Acid.** This sugar, obtained, *together with* carmine-red, by boiling carminic acid with dilute sulphuric acid (p. 414), has the composition $C^6H^{10}O^5$ when dried at 50°, $C^6H^8O^4$ at 100°. It is a honey-yellow, amorphous, hygroscopic mass, having a faint odour of caramel and a *bitterish* taste; dissolves very slightly in alcohol; easily reduces cupric oxide in alkaline solution; exhibits, even in very small quantity, Pettenkofer's bile reaction; is unfermentable and optically inactive (Hlasiwetz a. Grabowski).

7. **Rhamnegin-sugar.** A kind of sugar isomeric with mannite, $C^6H^{14}O^6$, obtained, together with rhamnetin, by boiling rhamnegin with dilute sulphuric acid:

$$C^{24}H^{32}O^{14} + 3H^2O = C^{12}H^{10}O^5 + 2C^6H^{14}O^6.$$

It is uncrystallisable and very sweet, dries up in a vacuum to a soft, amorphous, very hygroscopic, deliquescent mass, turns brown at 100°, and gives off *1 mol. water*, leaving a residue which has the composition $C^6H^{10}O^5$. It is dextrogyrate: [α] about = 26° (Schützenberger, *Compt. rend.* lxvii. 176).

8. **Dambonite** and **Dambose.** Dambonite, $C^4H^8O^3$, is a crystallisable sugar existing ready-formed in Gaboon caoutchouc; and dambose, $C^3H^6O^3$ or $C^6H^{12}O^6$, is formed from it, together with methyl iodide, by the action of hydriodic acid (p. 541).

SUGAR-CANE. Elaborate investigations on the sugar-cane, the extraction of the juice from it, the composition of the juice, and the changes to which it is liable, have been made by Icery (*Ann. Ch. Phys.* [4] v. 350; abstr. *Jahresb.* 1865, *p. 818*).

SULPHACETIC ACID, $CH^2\left\{\begin{matrix}SO^2OH\\COOH\end{matrix}\right.$, is formed, as potassium salt, by boiling monochloracetic acid with a solution of potassium sulphate (Strecker, *Zeitschr. f. Chem.* [2] iv. 214):

$$CH^2Cl.COOK + KSO^3K = KCl + CH^2\left\{\begin{matrix}SO^2OK\\COOK\end{matrix}\right.$$

SULPHACETONE, C^3H^6S, or rather the polymeric compound $C^6H^{12}S^2$, is formed by the action of 1 mol. phosphorus trisulphide on 6 mol. acetone, the action beginning at ordinary temperatures, and being completed at the heat of the water-bath. The upper layer of liquid thereby produced yields sulphacetone by fractional distillation, as a yellowish oil boiling between 183° and 185° (corr.), and having a vapour-density = 5·0787 (calculation for $C^6H^{12}S^2$ gives 5·114). It irritates the skin, and its vapour attacks the eyes very strongly (Wislicenus, *Zeitschr. f. Chem.* [2] v. 324).

SULPHAMMONIC ACIDS (Claus a. Koch, *Zeitschr. f. Chem.* [2] v. 684).—The potassium salts of these acids—Frémy's *sulphazotised acids* (v. 482)—are produced by the mutual action of nitrite and sulphite of potassium. When neutral solutions of these two salts are mixed together, the mixture becomes turbid after a while, and deposits slender needle-shaped crystals, the liquid at the same time acquiring an alkaline reaction. The crystals sometimes consist of a single salt, sometimes of a mixture of several, according to the proportions of the sulphate and nitrite added and the concentration of the solution. When the sulphite is in considerable excess, only one salt is formed, viz. potassium tetrasulphammonate, $K^4HNS^4O^{12} + 3H^2O$:

$$4K^2SO^3 + KNO^2 + 3H^2O = 5KHO + K^4HNS^4O^{12}.$$

This salt crystallises in needles. It is very unstable, cannot be kept long even in the dry state, and decomposes in a few minutes when washed on a filter with water, the water acquiring an acid reaction. Under an alkaline solution it is more permanent, but even then it decomposes quickly when heated even to temperatures short of the boiling point. By addition of acids the decomposition is still further accelerated; but complete decomposition, resulting in the formation, not of another sulphazotised acid, but of sulphuric acid, takes place only after prolonged boiling with dilute acids, or after heating with a concentrated acid. In neither of these cases is any oxide of nitrogen reproduced, but the whole of the nitrogen passes into the form of ammonia. The hydrated salt, when quickly heated, suffers complete decomposition, leaving potassium sulphate; the anhydrous salt heated above 200° gives off ammonium sulphate, nitrogen, and sulphurous oxide; by dry distillation with soda-lime all the nitrogen is eliminated as ammonia.

In the cases above mentioned of spontaneous decomposition of the dried substance, decomposition by prolonged contact with water, or by boiling with dilute potash, 1 mol. of the tetrasulphammonate is always resolved into 1 mol. of acid potassium sulphate, and 1 mol. of potassium trisulphammonate, $K^3H^2NS^3O^9$ (Frémy's sulphammonate). In the decomposition by water the reaction is

$$K^4HNS^4O^{12} + H^2O = KHSO^4 + K^3H^2NS^3O^9;$$

in boiling with potash, neutral potassium sulphate is of course obtained instead of the acid sulphate. The best way of preparing this salt is to mix 3 eq. of potassium sulphite with 1 eq. of the nitrite, and after about an hour, when the tetrasulphammonate has separated, and the alkaline reaction has become strong, to warm the mixture in the water-bath. The whole of the crystals then generally dissolve; if not, a little water must be added till a clear solution is formed, and from this the trisulphammonate separates in fine crystals on cooling. Pure potassium trisulphammonate, when decomposed at a high temperature, yields (contrary to Frémy's statement) not a trace of any oxide of nitrogen, the products of its decomposition being potassium sulphate, sulphuric acid, ammonium sulphate, and sulphurous acid. Strong sulphuric acid and nitric acid act on it but slowly in the cold, and when heated dissolve it without evolution of gas, forming the sulphates of potassium and ammonium. A solution of the trisulphammonate in water at 30°–40° forms with basic lead acetate a thick white precipitate, which, however, is not of constant composition. It does not appear to form an insoluble salt by double decomposition with any other metallic salt.

The trisulphammonate boiled with pure, or, better, with slightly acidulated water, splits up into acid sulphate and disulphammonate of potassium:

$$K^3H^2NS^3O^9 + H^2O = KHSO^4 + K^2H^3NS^2O^6.$$

This last salt, identical with Frémy's sulphamidate, separates on cooling from a hot aqueous solution in very characteristic forms; a drop of the hot solution left to cool under the microscope exhibits at first regular six-sided tables, changing afterwards to six-sided prisms having the character of augite crystals. They are anhydrous, and may be heated to 150° without alteration. It is scarcely attacked by strong sulphuric acid in the cold, but dissolves in it when heated, and is converted into the sulphates of potassium and ammonium. It is very sparingly soluble in cold water, and instantly crystallises from a hot aqueous solution on the addition of a few drops of potash. From concentrated, hot-saturated solutions, neutral lead acetate throws down a white precipitate; basic lead acetate also from very dilute solutions.

The other sulphazotised salts, designated by Frémy as *sulphazates*, *sulphazotates*, &c., have not been obtained pure, but they appear to differ essentially in constitution from the sulphammonates, inasmuch as when boiled with water, or heated in the air, or with sulphuric or nitric acid, they give off nitrogen dioxide, and when heated with soda-lime, give off only part of their nitrogen as ammonia, or in most cases do not yield any ammonia.

See further Claus (*Deut. chem. Ges. Ber.* iv. 186, 504; *Chem. Soc. J.* [2] ix. 307, 659).

SULPHOBENZENE or **SULPHOBENZIDE.** See Benzene, Derivatives of (p. 276).

SULPHOBENZOLAMIDE. $C^6H^7NSO^2 = NH^2(SO^2C^6H^5)$.—This compound, which Stenhouse obtained by heating ammonium phenylsulphite to 200° (v. 489), is also produced by the action of ammonia on sulphobenzol-bromide or phenylsulphurous bromide, $C^6H^5SO^2Br$. It is nearly insoluble in cold water, more soluble in hot ammoniacal water, easily soluble in hot alcohol and in ether, and crystallises in large nacreous laminæ melting at 149° (Otto a. Ostrop, *Ann. Ch. Pharm.* cxli. 365; *Jahresb.* 1866, p. 570).

SULPHOBENZOLIC ACID. See Benzene, Derivatives of (p. 273).

SULPHOCARBAMIC ACID. $CH^3NS^2 = CS\left\{\begin{matrix}NH^2\\SH\end{matrix}\right.$ (Mulder a. Wefers Bettinck, *J. pr. Chem.* ciii. 178; *Zeitschr. f. Chem.* [2] iv. 376).—In the ordinary mode of preparing ammonium sulphocarbamate (v. 490), the sulphocarbonate is likewise formed more or less abundantly at the beginning of the reaction; but if the ammonia-gas from 150 pts. of sal-ammoniac be passed into 600 pts. of alcohol of 95 p. c., 96 pts. of bisulphide then added, and the solution left to crystallise, the crystals deposited consist wholly of sulphocarbamate. On gradually adding hydrochloric acid to a concentrated solution of ammonium sulphocarbamate, sulphocarbamic acid is sometimes deposited in colourless needle-shaped crystals, especially if the solution be slightly cooled.

Sulphocarbamic acid is solid at ordinary temperatures, very soluble in water, alcohol, and ether; the solutions have an acid reaction. The acid is rather unstable; its alcoholic solution gradually deposits crystals of ammonium sulphocarbamate, and on heating it, carbon bisulphide is given off, and ammonium *sulphocarbamate* (insoluble in alcohol) is immediately formed:

$$2CS\left\{\begin{matrix}NH^2\\SH\end{matrix}\right. = CS^2 + CS\left\{\begin{matrix}NH^2\\S(NH^4)\end{matrix}\right..$$

The same decomposition takes place when the aqueous solution is heated; on evaporating it, a large quantity of ammonium sulphocyanate is formed:

$$CS\left\{\begin{matrix}NH^2\\S(NH^4)\end{matrix}\right. = H^2S + S\left\{\begin{matrix}CN\\NH^4\end{matrix}\right..$$

On *Sulphocarbamate of Acetonine*, see Acetonine (p. 29).

Action of Iodine on Sulphocarbamates.—When a strong alcoholic solution of iodine is poured into an alcoholic solution of ammonium sulphocarbamate, the colour of the iodine disappears, sulphur is deposited, and ethyl-sulphocarbimide is formed, together with ethylamine:

$$\underset{\substack{\text{Ammonium}\\\text{sulphocarbamate.}}}{CS\left\{\begin{matrix}NH^2\\SNH^4\end{matrix}\right.} + \underset{\text{Alcohol.}}{2C^2H^5OH} + I^2 = \underset{\substack{\text{Ethyl-sulpho-}\\\text{carbimide.}}}{N\left\{\begin{matrix}CS\\C^2H^5\end{matrix}\right.} + \underset{\text{Ethylamine.}}{N\left\{\begin{matrix}C^2H^5\\H^2\end{matrix}\right.} + 2H^2O + 2HI$$

(Hofmann, *Zeitschr. f. Chem.* [2] v. 671).

Action of Aldehydes.—When an alcoholic or aqueous solution of acetic aldehyde is agitated with ammonium sulphocarbamate, carbothialdine is produced, which, therefore, has the composition of *diethylidenammonium sulphocarbamate*:

$$\underset{\text{Aldehyde.}}{2C^2H^4O} + \underset{\substack{\text{Ammonium-}\\\text{sulphocar-}\\\text{bamate.}}}{CS\left\{\begin{matrix}NH^2\\S(NH^4)\end{matrix}\right.} = \underset{\text{Carbothialdine.}}{CS\left\{\begin{matrix}NH^2\\SN(C^2H^4)^2\end{matrix}\right.} + 2H^2O.$$

In the decomposition of carbothialdine, aldehyde is always reproduced. The homologous compound, *diamylidenammonium sulphocarbamate*, $CS\left\{\begin{matrix}NH^2\\SN(C^5H^{10})^2\end{matrix}\right.$, is obtained by agitating ammonium sulphocarbamate with valeral in alcoholic solution, and pouring the filtered liquid into water, as a colourless flocculent precipitate, which after washing with water, pressing between paper, and drying in a vacuum, forms a shining crystalline mass. Heated with ferric chloride it gives the sulphocyanogen reaction. *Diallylidenammonium sulphocarbamate*, $CS\left\{\begin{matrix}NH^2\\SN(C^3H^4)^2\end{matrix}\right.$, obtained by agitating acrolein with ammonium sulphocarbamate in aqueous solution in a cooled vessel, is colourless, apparently amorphous, insoluble in water and alcohol; gives the sulphocyanogen reaction when heated with ferric chloride (Mulder a. Bettinck).

Ethyl sulphocarbamate, $CS\left\{\begin{matrix}NH^2\\SC^2H^5\end{matrix}\right.$, is formed by the action of hydrogen sulphide on ethyl sulphocyanate. It is converted by the fixed alkalis into ethyl sulphide and metallic sulphocyanate; by ammonia into ethyl sulphide and sulphocarbamide, isomeric with ammonium sulphocyanate. A mixture of ethyl sulphocarbamate and ethyl iodide solidifies to a crystalline mass, apparently consisting of a compound of the two in equivalent proportions. The iodides of methyl and amyl, as well as the bromides of the same radicles, react in the same manner with the sulphocarbamates of ethyl and its homologues (Jeanjean, *Jahresb.* 1866, p. 501).

Ethyl-sulphocarbamic Acid. $C^3H^7NS^2 = CS\left\{\begin{matrix}NH(C^2H^5)\\SH\end{matrix}\right.$.—An alcoholic solution of ethylamine mixed with carbon bisulphide becomes hot, loses its alkaline reaction, and, if sufficiently concentrated, deposits six-sided tables of ethylsulphocarbamate of ethyl-ammonium:

$$2N(C^2H^5)H^2 + CS^2 = CS\left\{\begin{matrix}NH(C^2H^5)\\SN(C^2H^5)H^3\end{matrix}\right..$$

This salt melts at 103°, and partly sublimes without decomposition when gently heated. It is soluble in water and easily soluble in alcohol. With caustic soda it gives off ethylamine, and is converted into sodium ethylsulphocarbamate, which, on addition of hydrochloric acid, yields ethylsulphocarbamic acid in oily drops floating on the surface, and solidifying after a while to fatty crystals, On adding more hydrochloric acid, the oily drops dissolve, with evolution of carbon bisulphide, and nothing but ethylamine hydrochloride remains in solution. Ethyl-ammonium ethylsulphocarbamate is decomposed when heated to 100°, and more easily when its alcoholic solution is heated under pressure to 110°–120°, giving off hydrogen sulphide, and leaving diethylsulphocarbimide, in the form of an oily liquid, which soon solidifies to crystals:

$$CS\left\{\begin{matrix}NH(C^2H^5)\\SNH^3(C^2H^5)\end{matrix}\right. = H^2S + N^2\left\{\begin{matrix}(C^2H^5)^2\\CS\\H^2\end{matrix}\right..$$

Ethylsulphocarbamic acid in the free state resolves itself into its components, ethylamine and carbon bisulphide; but its metallic salts, especially in presence of excess of another metallic salt (*e.g.* silver nitrate or mercuric chloride), are easily resolved into ethyl-sulphocarbamide and a metallic sulphydrate (p. 1050):

$$CS\left\{\begin{matrix}NH(C^2H^5)\\SM\end{matrix}\right. = N\left\{\begin{matrix}CS\\C^2H^5\end{matrix}\right. + HMS.$$

The corresponding *methyl-* and *amyl-*compounds are obtained by similar processes, and exhibit similar reactions (Hofmann, *Zeitschr. f. Chem.* [2] iv. 686; *Jahresb.* 1868, p. 653).

Ethylic Ethyl-oxysulphocarbamate, Ethyl-xanthamide, or *Semi-sulphuretted Ethyl-urethane*, $CS\left\{\begin{matrix}NH(C^2H^5)\\OC^2H^5\end{matrix}\right.$, is produced by direct combination of ethyl-sulphocarbimide, $N(CS)(C^2H^5)$, and ethyl-alcohol, $HO(C^2H^5)$, when the two are heated together to 110° in a sealed tube for several hours, and is precipitated on mixing the resulting liquid with water, as an oil having a somewhat unpleasant alliaceous odour, and boiling, after purification, at 204°–208°. Under the influence of water, and especially in presence of acids or alkalis, it is resolved into alcohol, carbon dioxide, hydrogen sulphide, and ethylamine. With strong sulphuric acid, carbon oxysulphide is formed instead of carbon dioxide and hydrogen sulphide. The above-described compound is likewise produced by the action of alcoholic soda-solution on ethyl-sulphocarbimide; but the corresponding sodium salt is always produced at the same time by the action of the sodium hydrate, and ultimately part of the ethylsulphocarbimide is completely decomposed, with formation of sodium carbonate, sodium sulphide, and ethylamine.

A compound isomeric with the preceding, and differing from it only in the relative position of the sulphur and oxygen atoms, is produced by heating ethylic mercaptan with ethyl cyanate to 120°. This body, $CO\left\{\begin{matrix}NH(C^2H^5)\\ SC^2H^5\end{matrix}\right.$, is heavier than water, has the same odour as the preceding, and likewise boils at 204°–208°. By the action of water, especially in presence of acids or alkalis, it is resolved into mercaptan, carbon dioxide, and ethylamine.

Ethylic Ethylsulphocarbamate, Diethyl-xanthamide, or *Sulphuretted Ethyl-urethane*, $CS\left\{\begin{matrix}NH(C^2H^5)\\ SC^2H^5\end{matrix}\right.$, is produced by digesting mercaptan with ethyl-sulphocarbimide to 120° for several hours. It is heavier than water, and does not exhibit the odour of either of its constituents. It is decomposed by distillation (Hofmann, *Zeitschr. f. Chem.* [2] v. 268).

Ethylic Allyl-oxysulphocarbamate, $CS\left\{\begin{matrix}NH(C^3H^5)\\ OC^2H^5\end{matrix}\right.$, obtained by digesting an alcoholic solution of mustard-oil for some hours to a temperature a little above the boiling point of water, and precipitating with water, is an oil having an alliaceous odour, somewhat heavier than water, and boiling at 210°–215°. It is the same compound that Will a. Körner obtained (v. 518) by treating mustard-oil with alcoholic potash, and to which they assigned the formula $C^{14}H^{25}N^3S^2O^2$ (Hofmann).

Ethylic Phenyloxysulphocarbamate, $CS\left\{\begin{matrix}NH(C^6H^5)\\ OC^2H^5\end{matrix}\right.$, is produced in like manner by heating phenylsulphocarbimide with alcohol to 110°–115°. The resulting solution poured into water solidifies to a crystalline mass, which may be purified by washing with water and recrystallisation from alcohol. It is resolved by distillation into its constituents. The same compound may be obtained, though less easily, from diphenylsulphocarbamide, which is the starting point for the preparation of phenyl-sulphocarbimide (p. 1056).

Ethylic Phenylsulphocarbamate or *Sulphuretted Phenyl-urethane*, $CS\left\{\begin{matrix}NH(C^6H^5)\\ SC^2H^5\end{matrix}\right.$, is produced by the combination of mercaptan with phenyl-sulphocarbimide. It is a finely crystallised compound, insoluble in water, soluble in alcohol and ether, melting at 56° (Hofmann).

SULPHOCARBAMIDES (Hofmann, *Zeitschr. f. Chem.* [2] iv. 201, 686; v. 157).—*Ethyl-sulphocarbamide*, $N^2\left\{\begin{matrix}CS\\ C^2H^5\\ H^3\end{matrix}\right.$, is formed by direct addition of ammonia in alcoholic solution to ethyl-sulphocarbimide, $N(CS)(C^2H^5)$ (p. 1055), and solidifies to a crystalline mass which by recrystallisation from hot water is converted into beautiful needles. It melts at 100°, is moderately soluble in water and more easily in alcohol, dissolves also in hydrochloric acid, and forms a yellow precipitate with platinic chloride. It is easily desulphurised, either in aqueous or in alcoholic solution, by lead oxide or mercuric oxide; and on evaporating the resulting solution over the water-bath, there remains a syrupy liquid which solidifies after some time to a network of crystals having a strong alkaline reaction. It is probable, however, that an intermediate product is first formed, as the liquid, especially if diluted, does not exhibit alkaline reaction immediately after desulphuration. The white crystals, although very soluble, must be recrystallised either from water or from alcohol. Their solution in the smallest possible quantity of hydrochloric acid gives with platinic chloride a crystalline platinum salt consisting of $C^3H^3(C^2H^5)^3N^6.2HCl.PtCl^4$. Probably the first product of the desulphuration is ethylcyanamide: $N^2(CS)H^3(C^2H^5) - H^2S = N(CN)(C^2H^5)H$; and three molecules of this compound then unite to form the biacid base: $3N(CN)(C^2H^5)H = C^3H^3(C^2H^5)^3N^6$, which may be regarded as melamine, $C^3H^6N^6$, having 3 at. hydrogen replaced by ethyl (p. 808).

Diethyl-sulphocarbamide, $N^2(CS)''(C^2H^5)^2H^2$, is produced by addition of ethylamine to ethylsulphocarbimide, also with evolution of hydrogen sulphide, by the decomposition of ethylammonium ethyl-sulphocarbamate (p. 1049). It forms crystals melting at 77°, soluble in alcohol, less soluble in water; dissolves also in hydrochloric acid, and gives a yellow crystalline precipitate with platinic chloride. By phosphoric anhydride or anhydrous hydrochloric acid it is resolved into ethylamine and ethylsulphocarbimide. It is not decomposed in aqueous or alcoholic solution by lead oxide, but recently

PSEUDOSULPHOCYANATES. See SULPHOCYANATES.

PTEROLITE. A mineral occurring in the Brevig Sound in Norway, together with pitch-black mica, astrophyllite, wöhlerite, and ægirin. It is massive and composed of numerous lamellæ, grouped like the beard of a feather and partly curved. Hardness = 2·5 to 3. Sp. gr. 3·063 to 3·666. Colour olive-green and liver-brown; lustre nacreous. Translucent only at the edges. An analysis by R. Müller gave

SiO^2	Al^2O^3	CaO	MgO	K^2O	Na^2O	FeO	Fe^2O^3	H^2O	
39·38	6·65	5·47	0·56	7·86	2·81	16·43	19·89	1·39	= 100·44

(Breithaupt, *Jahrb. Min.* 1865, p. 858; *Jahresb.* 1865, p. 887).

PURPURIN. According to the recent investigations of Strecker (*Zeitschr. f. Chem.* [2] iv. 265), and of Graebe a. Liebermann (*ibid.* 503), this substance has the composition of oxyalizarin, $C^{14}H^8O^5$. For Bolley's experiments on the composition of purpurin and other madder colours, see *Dingl. pol. J.* clxxxii. 351; *Jahresb.* 1866, p. 643. For E. Kopp's method of preparing purpurin, &c., from madder, see *Bull. Soc. industr. de Mulhouse*, xxxvii. 437; *Jahresb.* 1867, p. 955.

PURPUROGALLIN. $C^{20}H^{16}O^9$ (A. Girard, *Compt. rend.* lxix. 865; *Zeitschr. f. Chem.* [2] vi. 86).—A red colouring matter produced by oxidation of pyrogallic acid with silver nitrate in alcoholic solution, or more conveniently with permanganic acid. 60 grams of potassium permanganate are dissolved in a litre of water mixed with 55 grams of hydrogen sulphate, and this solution is gradually poured into a strong aqueous solution containing 40 grams of pyrogallic acid. Purpurogallin then separates in orange-red flocks, which may be purified by washing with a little water and crystallisation from alcohol, or by sublimation. It sublimes at about 200° in garnet-red needles, having a finer colour and stronger lustre than alizarin. It dissolves sparingly in water, more easily in alcohol, also in ether and in benzol, forming yellow solutions. Sulphuric acid dissolves it, forming a compound which crystallises in crimson needles decomposed by water. Most other acids dissolve it without alteration. Nitric acid attacks it energetically; the very concentrated acid may even set it on fire; ordinary nitric acid converts it into picric acid. Alkalis impart to the solutions of pyrogallin a transient blue colour; aluminium sulphate, on addition of ammonia, throws down a violet-blue lake, which gradually turns brown. Lead acetate forms a red-brown precipitate. Silver nitrate colours the solutions violet-blue, then brown, with separation of metallic silver. Auric chloride forms a bright carmine-red solution, which however also turns brown and deposits metallic gold. Purpurogallin dyes mordanted fabrics quickly and completely, but the colours are not very good.

PYRIDINE. C^5H^5N.—According to Chapman a. Smith (*Ann. Ch. Pharm. Suppl.* vi. 329; *Jahresb.* 1868, 682), this base is formed by dehydration of amyl nitrite, *e.g.* when that compound is heated with phosphoric anhydride, $C^5H^{11}NO^2 - 3H^2O = C^5H^5N$.

Dipyridine. $C^{10}H^{10}N^2$ (Anderson, *Chem. Soc. J.* [2] vii. 406).—This base, polymeric with pyridine, is formed, together with other products, by the action of sodium on pyridine. When dry pyridine is heated to its boiling point with small pieces of sodium amounting to about one-fifth of its weight, in a flask furnished with a long condensing-tube, the whole is gradually converted into a dark brown or black mass, which solidifies on cooling to a hard brittle resin; and on separating this resin as completely as possible from unaltered sodium, and throwing it by small pieces into water, it is slowly converted into a thick brown oil, which collects at the bottom of the vessel, and when washed with water, dried with calcium chloride, and distilled in a current of hydrogen, yields at first a light oil consisting of several bases, then a thick heavy oil which deposits crystals of dipyridine. On redistilling this product, dipyridine crystallises in the neck of the retort, and the fluid portions of the distillate yield a further quantity of it when cooled by a freezing mixture. The formation of dipyridine by the action of sodium on pyridine takes place also in the cold. In this case, the sodium becomes covered, in the course of a few days, with a black brittle crust, which when washed with pyridine to remove an oil formed at the same time, then detached as completely as possible from the sodium, and thrown into water, yields a dark grey powder, which falls to the bottom. This powder washed till free from soda, and then spread out in contact with the air, is entirely converted into a snow-white mass of interlaced acicular crystals, consisting of dipyridine.

Dipyridine melts at 108°; solidifies to a crystalline mass on cooling; volatilises slowly at 100°; and sublimes unchanged at a high temperature, in long needle-shaped

SULPHOCYANIC ACID. $CHNS$.—On the preparation of this acid, see Hermes (*J. pr. Chem.* xcvii. 465).

Sulphocyanic acid is reduced by zinc and excess of dilute sulphuric acid, yielding hydrogen sulphide and methylamine (Merz a. Weith, *Zeitschr. f. Chem.* [2] iv. 611):

$$CSNH + 6H = H^2S + CH^3NH^2.$$

According to Hofmann (*ibid.* 689), the products are ammonia, formic sulphaldehyde, CH^2S, hydrocyanic acid, hydrogen sulphide, and methylamine, produced in the following order:

$$\begin{array}{rl} \text{I.} & CSNH + 2H^2 = H^3N + CH^2S \\ \text{II.} & CSNH + H^2 = CNH + H^2S \\ \text{III.} & CNH + 4H = CH^3NH^2 \end{array}$$

(Hofmann, *ibid.* 688).

Metallic Sulphocyanates. Many metallic sulphocyanates are soluble in ether, and this property may be made available for their preparation. When the [illegible] liquid produced by mixing potassium sulphocyanate with a cobalt salt is shaken up with ether, the ether immediately becomes blue, and deposits on evaporation crystals of cobalt sulphocyanate. The blue colour, which is also produced with alcohol, is destroyed by mercuric chloride and by sodium acetate and hyposulphite. Ethereal solutions of the sulphocyanates of iron, uranium, molybdenum, tungsten, gold, and copper may be obtained in the same manner. The iron salt dissolves so easily that it may be completely extracted by ether from its aqueous solution (Skey, *Chem. News*, xvi. 201).

Ammonium sulphocyanate, $CSN(NH^4)$, is often present in commercial ammonium sulphate. An alcoholic solution of this salt exhibits in a very high degree the phenomenon of supersaturation. Its concentrated aqueous solution does not dissolve sulphur, but takes up a considerable quantity of iodine, and on heating the resulting liquid, a considerable quantity of persulphocyanogen is deposited. Bromine acts in a similar manner. Chlorine forms no precipitate in the dilute solution, but throws down from the concentrated solution a thick yellow precipitate of persulphocyanogen, agreeing in composition with Völckel's analyses (iv. 380) (Phipson, *Chem. News*, xviii. 109). Ammonium sulphocyanate melts at 159° (not at 147°, as generally stated), and if kept for some time at the temperature of 170°, is converted into sulphur-urea, CH^4N^2S (J. E. Reynolds, *Chem. Soc. J.* [2) vii. 1).

Chromic Sulphocyanates (Roesler, *Ann. Ch. Pharm.* cxli. 185; *Zeitschr. f. Chem.* [2] ii. 615).—*Potassio-chromic sulphocyanate*, $(CNS)^{12}Cr^{vi}K^6 + 8H^2O$, is obtained by heating the moderately concentrated solutions of 6 pts. potassium sulphocyanate and 5 pts. chrome-alum nearly to the boiling point for about two hours, mixing the cooled liquid with alcohol to precipitate sulphates, evaporating the filtrate, and recrystallising the salt thereby separated from alcohol. It forms nearly black crystals belonging to the quadratic system, ruby-red by transmitted light. It is permanent in the air, gives off its water at 100°, becomes dark-coloured when heated, ruby-red again on cooling; dissolves in 0·72 pts. water, and in 0·94 pts. alcohol. It is not altered by alkaline carbonates or ammonium sulphide even at the boiling heat: but on warming it with soda-ley, or boiling it with ammonia, chromic oxide is separated. Dilute hydrochloric acid decomposes it at the boiling heat; strong hydrochloric acid throws down, together with potassium chloride, a yellow sulphuretted powder, which crystallises from alcohol in needles. By evaporation with hydrochloric acid, the salt is completely decomposed, with formation of chromic chloride and potassium chloride. Nitric acid oxidises it with facility. The salts of the alkaline earth-metals, and those of cadmium, cobalt, nickel, zinc, manganese, and iron, are precipitated by potassio-chromic sulphocyanate. Cupric sulphate changes its wine-red colour to violet-blue, and on standing or warming forms a brown precipitate containing copper. Mercuric chloride forms a red precipitate which agglomerates at the boiling heat; mercurous salts form a yellow precipitate gradually turning green; tin-salts a white precipitate.—The *ammonium salt*, $(CNS)^{12}Cr^{vi}(NH^4)^6 + 8H^2O$, is formed, with evolution of ammonia, when recently precipitated chromic hydrate is heated with ammonium sulphocyanate, but is more advantageously prepared like the potassium salt, namely by mixing a solution of 1 pt. ammonium dichromate, reduced by alcohol with addition of sulphuric acid and neutralised with ammonia, with 3 pts. of ammonium sulphocyanate, and heating the liquid to the boiling point.—The *sodium salt*, $(CNS)^{12}Cr^{vi}Na^6$, prepared by boiling a neutralised solution of chromic sulphate with sodium sulphocyanate, evaporating and treating the residue with alcohol, crystallises in thin, deliquescent laminæ, having a lighter colour than the other double chromic sulphocyanates.—The *barium salt*, $(CNS)^{12}Cr^{vi}\overset{\prime\prime}{Ba}{}^3$, prepared by mixing a neutral solution of chromic chloride with barium sulphocyanate, crystallises in deliquescent, ruby-coloured, short, four-sided prisms.—The *silver salt*, $(CNS)^{12}Cr^{vi}Ag^6$, is a brown-red, bulky precipitate, retaining, when dried over oil of vitriol, 53·9 p. c. water, which it gives off at 100°, the salt assuming a pale red colour. It is but imperfectly oxidised even by fuming nitric acid, is insoluble in ammonia, but dissolves with deep cherry-red colour in potassium cyanide. When suspended in water, it is decomposed by caustic soda and by hydrogen sulphide.—The *lead salt*, $(CNS)^{12}Cr^{vi}\overset{''}{Pb}{}^3.4PbH^2O^2 + 8H^2O$, obtained by precipitation with lead acetate, has a rose-red colour, and when washed with water gives up lead sulphocyanate and is converted into $(CNS)^{10}Cr^{vi}\overset{''}{Pb}{}^2.4PbH^2O^2 + 5H^2O$. By boiling with water it is completely resolved into lead sulphocyanate, which dissolves, and a mixture of chromic oxide and lead oxide.—*Hydrochromic Sulphocyanate* or *Chromi-sulphocyanic acid*, $(CNS)^{12}Cr^{vi}H^6$, is obtained, by decomposing the lead salt with hydrogen sulphide, as a deep wine-red, strongly acid liquid, which, when evaporated, gives off sulphocyanic acid, and leaves green, deliquescent *chromic sulphocyanate*, $(CNS)^6Cr^{vi}$ (v. 506).

Lithium Sulphocyanate, obtained by saturating the acid with lithium carbonate, crystallises over oil of vitriol in very deliquescent laminæ. The *glucinum salt* crystallises less easily, and, like the preceding salt, is soluble in alcohol (Hermes, *J. pr. Chem.* xcvii. 465; *Jahresb.* 1866, p. 294).

Mercury Sulphocyanates (J. Philipp, *Pogg. Ann.* cxxxi. 86; *Jahresb.* 1867, p. 376;—Hermes, *loc. cit.*).—The white precipitate of *mercuric sulphocyanate*, $(CNS)^2Hg$, formed by adding potassium sulphocyanate to mercuric nitrate, is soluble in excess of either salt. From boiling water or from a hot solution of mercuric oxide in sulphocyanic acid, it crystallises in nacreous laminæ (Philipp). It dissolves in cold hydrochloric acid and aqueous metallic chlorides, less easily in hot water, alcohol, and ether; decomposes at 165°, and explodes violently when triturated with potassium chlorate. Boiled with hydrochloric acid, it forms a yellow amorphous body, which is decomposed by boiling water into mercuric sulphide and hydrochloric acid. A solution of mercuric sulphocyanate in sulphocyanic acid deposits on evaporation yellow needle-shaped crystals of *hydromercuric sulphocyanate*, $(CNS)^2Hg.2CNSH$ (Hermes). *Potassio-mercuric sulphocyanate*, $(CNS)^3HgK$, is obtained by adding mercuric nitrate to potassium sulphocyanate till the white precipitate formed at first is converted into a yellow, crystalline mass, and then warming; or by directly dissolving mercuric sulphocyanate in potassium sulphocyanate. It is moderately soluble in warm water, but is decomposed by a large quantity of cold water, with separation of mercuric sulphocyanate. The compound $(CN)^2Hg.CNSK + 2H^2O$, originally obtained by Böckmann (*Ann. Ch. Pharm.* xxii. 153), separates on mixing the concentrated solutions of its component salts, as a crystalline pulp; from dilute solutions in nacreous laminæ or slender prisms; the solution is not precipitated by potash or ammonia. The compound $HgI^2.2CNSK + 2H^2O$ crystallises from a saturated solution of mercuric iodide in potassium sulphocyanate, as a yellowish, deliquescent salt, which, as well as the saturated solution, is decomposed by water, with separation of yellow mercuric oxide, which gradually changes to the red modification. Mercuric iodide dissolves, however, in a very dilute solution of potassium sulphocyanate. A solution containing mercuric chloride or bromide, together with excess of potassium sulphocyanate, first deposits chloride or bromide of potassium, and afterwards the double sulphocyanate of potassium and mercury. Concentrated solutions of mercuric chloride and potassium sulphocyanate gradually deposit mercuric sulphocyanate; but, on the other hand, mercuric chloride is formed when mercuric sulphocyanate acts upon potassium chloride (Philipp). The yellow precipitate formed by ammonia in a solution of potassio-mercuric sulphocyanate, and regarded by Claus as a mercuric oxysulphocyanate (v. 508), consists, according to Philipp, of *mercurammonium oxysulphocyanate*, $NH^2Hg''.CNS.HgO$. This body detonates when heated, turns grey when exposed to light, and is coloured brown by potassium iodide.

Mercurous Sulphocyanate, $(CNS)^2Hg^2$, the existence of which is doubted by Hermes, is formed on adding potassium sulphocyanate to a large excess of dilute and somewhat acid mercurous nitrate. Small quantities of mercuric sulphocyanate and metallic mercury appear to be formed at first, but if the liquid is sufficiently acid, the grey or black precipitate becomes white after standing for some time, in consequence of the mercuric sulphocyanate uniting with the mercury to form the mercurous salt. Mercurous sulphocyanate is white, insoluble in water, blackened by alkalis; dissolves in hot hydrochloric acid, and in potassium sulphocyanate with separation of mercury, and behaves, when heated, like mercuric sulphocyanate, but does not swell up so much (Philipp).

Bromopyroracemic acids (mono- and di-) are formed by heating pyroracemic acid to 100° in a sealed tube with 1 or 2 mol. bromine and water. The *dibrominated acid* is more easily otained pure than the monobrominated acid, and may be extracted from the water by ether. It crystallises from aqueous solution in large rhombic tables, which contain $C^3H^2Br^2O^3 + H^2O$, and give off their 1 mol. water even on exposure to the air, more quickly in a vacuum. The effloresced acid crystallises from anhydrous solvents in long needles melting at 89°–91°. If the acid during its preparation be exposed for a long time to a high temperature, it is decomposed, with formation of pentabromacetone, C^3HBr^5O:

$$CHBr^2—CO—CO^2H + 3HBr = 2H^2O + CHBr^2—CO—CBr^3.$$

Dibromopyroracemic acid is decomposed by silver oxide, giving up all its bromine, and being converted in the cold, chiefly into mesoxalic acid, $C^3H^2O^5$; at a gentle heat silver is separated, and carbon dioxide is evolved. It is carbonised by alcoholic ammonia, but aqueous ammonia converts it into *imido-pyroracemic acid*, $CH(NH)—CO—CO^2H$. This compound possesses but slightly acid properties, and crystallises indistinctly; it unites directly with nitric acid, and gives with silver nitrate a white curdy precipitate, containing $C^3HAg(NH)O^3.AgNO^3$. *Monobromopyroracemic acid* has been obtained only as a syrupy liquid, which when treated with silver oxide, gives off carbon dioxide, as soon as the liquid becomes neutral, even at low temperatures. At a gentle heat silver acetate is produced (Wichelhaus, *loc. cit.*).

PYROTARTARIC ACID, $C^5H^8O^4$, is produced by heating pulverised tartaric acid to 180° in sealed tubes with hydrochloric acid (Geuther a. Riemann, *Zeitschr. f. Chem.* [2] v. 318); also, as above observed, by heating pyroracemates with acetates (Wichelhaus); also, together with several other products, by fusing gamboge with potash (Hlasiwetz a. Barth, p. 628).

The *chloro-*, *bromo-*, and *iodo- derivatives* of pyrotartaric acid are formed, not from that acid itself, but by direct addition of Br^2, Cl^2, I^2, or of HBr, HCl, HI, to the pyrocitric acids, $C^5H^6O^4$, and they exhibit different modifications, accordingly as they are formed from citraconic, itaconic, or mesaconic acid. (See Acids, Organic, p. 49.) The dibromo-compounds, obtained by addition of bromine to these acids, were discovered by Kekulé, and are described in vol. iv. pp. 773, 774. The monochlorinated, monobrominated, and monoiodated derivatives have been studied by Swarts (*Bull. Acad. Belg.* [2] xvii. xix.; *Instit.* 1865, p. 23; 1866, pp. 323, 358; *Jahresb.* 1865, p. 392; 1866, p. 404); they are formed by addition of HCl, HBr, and HI, to itaconic, citraconic, and mesaconic acid respectively.

Citramonochloropyrotartaric acid, $C^5H^7ClO^4$, formed by heating citraconic anhydride to 120° for two or three hours with an equal volume of strong hydrochloric acid, crystallises from ether in nacreous laminæ unctuous to the touch. Both in the dry state and in solution it is decomposed by the slightest elevation of temperature into hydrochloric and mesaconic acids. Heated with bases, it is resolved, like citradibromopyrotartaric acid, into carbon dioxide and crotonic acid:

$$C^5H^7ClO^4 = C^4H^6O^2 + HCl + CO^2.$$

In cold water it dissolves without decomposition, and the solution is not precipitated by silver nitrate; but on gently heating it, a precipitate of silver chloride is formed.

Itamonochloropyrotartaric acid is formed by heating pulverised itaconic acid to about 130° for three hours with 2 pts. of very strong hydrochloric acid, washing the product with cold water, and recrystallising from water or alcohol. It forms white lustreless nodules or crystals, like those of pyrotartaric acid, inodorous, and having an agreeable sour taste. It melts at 140°–145°, remaining liquid for a long time, and boils at 225°–230°, forming water, hydrochloric acid, and an oily anhydride which crystallises after a while, and is reconverted into the original acid. Heated to 150° in a stream of dry air, it gives off water, and leaves the anhydride, which, however, cannot be obtained pure, in consequence of simultaneous loss of hydrochloric acid. Hot water converts it into itamalic acid (p. 761):

$$C^5H^7ClO^4 + H^2O = HCl + C^5H^8O^5.$$

The same decomposition is produced by strong bases; but the solution saturated with ammonia deposits sal-ammoniac on evaporation, and the mother-liquor contains mesaconic acid. Treated with silver oxide, it yields, together with silver chloride, the silver salt of paraconic acid, isomeric with itaconic acid, but monobasic (p. 760). *Ethylic itachloropyrotartrate*, $C^5H^5Cl(C^2H^5)^2O^4$, is obtained, by saturating the alcoholic solution of the acid with hydrochloric acid gas, and rectifying the liquid precipitated by water, as a colourless bitter liquid, which boils at 250°–252°, with formation of a small quantity of hydrochloric acid.

Mesamonochloropyrotartaric acid is formed by repeatedly heating mesaconic acid to 160° with very strong hydrochloric acid. The solution of the product deposits on evaporation, first lustreless nodules of unaltered mesaconic acid, then small shining crystals of the much more soluble chlorinated acid. The latter melts at 129°–130°, and is resolved by boiling with water into hydrochloric and mesaconic acids. It is converted by bases into crotonic acid.

Itadichloropyrotartaric acid, $C^5H^6Cl^2O^4$, formed by addition of chlorine to itaconic acid, is very soluble, forms large crystals, and is decomposed by boiling its solution.

Itamonobromopyrotartaric acid, $C^5H^7BrO^4$, is prepared, like the chlorinated acid, by heating itaconic acid for half an hour to 160° with concentrated hydrobromic acid; also, though less advantageously, by the action of bromine on pyrotartaric acid at 120°; also by the action of fuming hydrobromic acid on itamalic acid: $C^5H^8O^5 + HBr = H^2O + C^5H^7BrO^4$. It melts at 130°–134°, remaining liquid for a long time, and boils without decomposition at about 250°. It is less easily decomposed by boiling water than the chlorinated acids, and reacts exactly like the latter with bases. *Ethyl itabromopyrotartrate* is obtained by heating the acid with alcohol to 110°; the product precipitated by water boils, with partial decomposition, at 270°–275°.

Itamoniodopyrotartaric acid, $C^5H^7IO^4$, is prepared by heating itaconic acid somewhat in excess with hydriodic acid to 150° in an atmosphere of carbon dioxide: if an excess of hydriodic acid be used, pyrotartaric acid will be likewise formed. The liquid purified from free iodine by treatment with mercury, deposits, on evaporation over sulphuric acid, dull nodular groups of crystals of the iodated acid (mixed with a little itaconic acid), which become colourless by repeated crystallisation from water. They melt at 135°, and decompose at 185°, with evolution of iodine. Boiling water produces only slow decomposition. The acid heated with hydriodic acid is reduced to pyrotartaric acid, with separation of iodine. Heated with alcohol containing hydrochloric acid, it yields ethylic itamono-iodopyrotartrate.

Citra-iodopyrotartaric acid cannot be isolated. When citraconic anhydride is heated with fuming hydriodic acid, a brown crystalline mass separates on cooling, which when submitted to purification, is resolved into hydriodic and mesaconic acids. Since however pyrotartaric acid is obtained by continued heating of citraconic anhydride with fuming hydriodic acid, it may be supposed that citra-iodopyrotartaric acid is formed as an intermediate product.

PYROTRITARTARIC ACID. $C^7H^8O^3$ (Wislicenus a. Stadnicki, *Ann. Ch. Pharm.* cxlvi. 306).—A crystalline acid formed, together with pyrotartaric acid, by the dry distillation of tartaric acid: $3C^4H^6O^6 = C^7H^8O^3 + 5CO^2 + 5H^2O$. It is obtained most abundantly by somewhat rapid distillation, but always in very small quantity, not exceeding 0·02 p. c. To separate it, the products distilling between 120° and 180° are subjected to repeated fractional distillation. Nearly pure pyrotartaric acid is then obtained between 160° and 170°, and between 180° and 210°, a series of gradually diminishing fractions, which as they cool partly deposit the pyrotritartaric acid in needle-shaped crystals. On dissolving these products in boiling water, whereby the admixed pyrotartaric anhydride is converted into pyrotartaric acid, and filtering at the boiling heat through wetted filters, the pyrotritartaric acid separates on cooling in yellowish needles, which may be purified by recrystallisation from boiling water with addition of animal charcoal. Pyrotartaric acid crystallises from the mother-liquors.

Pyrotritartaric acid forms colourless shining needles, soluble in about 400 pts. of boiling water, less soluble in cold water, easily soluble in alcohol and ether, and crystallising from the latter in short thick prisms. The solutions have a decided acid reaction. The acid melts at 134·5°, sublimes even below this temperature, in small needles, and easily passes over with vapour of water. The pyrotritartrates of the alkali-metals are easily soluble in water; probably also those of the alkaline-earth metals. The lead and silver salts are white precipitates, insoluble in water, and becoming crystalline when immersed therein.

The acid treated with phosphorus pentachloride is converted into the chloride $C^7H^7O^2Cl$, which, however, is immediately reconverted by water into pyrotritartaric acid. Wislicenus and Stadnicki regard this acid as a ketonic acid, $C^6H^7—CO—COOH$, although no hydrogen can be introduced into it by the action of sodium-amalgam. From its properties it might rather be supposed to belong to the aromatic group.

PYRRHENE. See AUGITE.

PYRROL. C^4H^5N. This compound may be prepared by heating ammonium mucate with glycerin in a retort to 180°–200°, the resolution of the ammonium salt

Methyl-sulphocarbimide, $N\left\{\begin{matrix}CS\\CH^3\end{matrix}\right.$, boils at 119°, melts at 34°, and solidifies at 26°. After distillation with aqueous vapour, it solidifies to a beautifully crystallised mass. Vapour-density obs. = 2·42; calc. 2·53.

Amyl-sulphocarbimide is best prepared by decomposition of the mercury salt of amyl-sulphocarbamic acid; but, instead of at once distilling off the product, it is better to cause the evolved vapours to condense and run back into the liquid for a considerable time. When the reaction is complete the mercuric sulphide is filtered off, and the amyl-sulphocarbimide is precipitated with water, dried over calcium chloride, and distilled. It is a liquid boiling at 183°–184°, and having an odour like that of the ethyl compound, but less powerful. Vapour density, obs. 4·4 (cal. 4·48) (Hofmann). According to Buff it boils at 182°, and has a sp. gr. of 0·957538 at 0°, 0·94189 at 17°, and 0·78749 at 182°.

Butyl-sulphocarbimide, $N\left\{\begin{matrix}CS\\C^4H^9\end{matrix}\right.$, constitutes the essential oil of common scurvy-grass or spoon-wort (*Cochlearia officinalis*), which is often confounded with oil of mustard. It boils at 159°–160°, and combines with ammonia, forming the splendidly crystallised compound *butyl-sulphocarbamide* or *butylic thiosinamine*, $N^2(CS)''(C^4H^9)H^3$, which melts at 135°.

Isobutylamine (prepared from butyl alcohol of fermentation) treated with carbon bisulphide and mercuric chloride yields a butyl-sulphocarbimide of the same composition and nearly the same boiling point as the preceding, but differing in odour and forming with ammonia a thiosinamine which melts at 90°; doubtless therefore *isobutyl-sulphocarbimide*, $N\left\{\begin{matrix}CS\\CH^2(CH)(CH^3)^2\end{matrix}\right.$.

Watercress yields a similar oil, apparently containing a radicle of very high order (Hofmann, *Zeitschr. f. Chem.* [2] v. 400).

Phenyl-sulphocarbimide. $N\left\{\begin{matrix}CS\\C^6H^5\end{matrix}\right.$.—The aromatic sulphocarbimides are not formed by decomposition of the metallic salts of phenyl-carbamic acid and its homologues. Phenyl-sulphocarbimide was originally obtained by the action of phosphoric anhydride on monophenyl-sulphocarbamide: $N^2(CS)(C^6H^5)H^3 = NH^3 + N(CS)(C^6H^5)$ (Hofmann, i. 756). It is also formed, together with triphenyl-guanidine, by the action of alcoholic iodine on a boiling alcoholic solution of diphenyl-sulphocarbamide (Hofmann), and by heating the same compound to 160°–170° with strong hydrochloric acid (Merz a. Weith). (See GUANIDINE, p. 655.) Heated with alcohol to a little above 100°, it forms *semi-sulphuretted phenyl-urethane*, $CS\left\{\begin{matrix}NH(C^6H^5)\\OC^2H^5\end{matrix}\right.$, and with mercaptan it forms *sulphuretted phenyl-urethane*, $CS\left\{\begin{matrix}NH(C^6H^5)\\SC^2H^5\end{matrix}\right.$ (Hofmann, p. 1050).

Tolyl-sulphocarbimide, $C^8H^7NS = \left\{\begin{matrix}CS\\C^6H^4(CH^3)\end{matrix}\right.$, is prepared by heating ditolyl-sulphocarbamide with phosphoric anhydride. Aromatic vapours are then evolved, which condense to a yellow, quickly crystallising oil. An admixture of ditolyl-sulphocarbamide may be removed by crystallisation from ether, in which tolyl-sulphocarbimide is extremely soluble. This compound crystallises in white needles a centimetre long, having an odour very much like that of anise oil. It dissolves easily in alcohol, sparingly in water, boils at 237°, melts at 26°, and resolidifies at 22°. Heated with *toluidine*, it forms ditolyl-sulphocarbamide; with *ammonia* it forms monotolyl-sulphocarbamide; with *aniline*, phenyl-tolylsulphocarbamide, which is easily obtained in fine crystals.

Benzyl-sulphocarbimide, $C^8H^7NS = N\left\{\begin{matrix}CS\\CH^2(C^6H^5)\end{matrix}\right.$, isomeric with the preceding, is produced, like the sulphocarbimides of the fatty series, by the action of mercuric chloride on benzyl-sulphocarbamate of benzylamine, inasmuch as benzylamine, $C^6H^5.CH^2(NH^2)$, is constituted like the amines of the fatty series, having the ammonia-residue NH^2 in the methyl group. On adding water to the distillate, the benzyl-sulphocarbimide separates in clear, heavy drops. It boils at 243°, and possesses in a high degree the odour of watercresses.

Menaphthylamine, treated with carbon bisulphide and mercuric chloride, likewise yields a sulphocarbamide.

All these compounds react like ethylic and allylic sulphocarbamides, especially with ammonia and amines (Hofmann).

Allyl-sulphocarbimide, or *Volatile oil of Mustard*, $N\left\{\begin{matrix}CS\\C^3H^5\end{matrix}\right.$.—It is remarkable that this compound, which exhibits all the essential characters of the sulphocarbimides above described, has not hitherto been produced artificially by analogous processes, but is obtained by a reaction which might rather be expected to yield allyl sulphocyanate, $S\left\{\begin{matrix}CN\\C^3H^5\end{matrix}\right.$, viz. by distilling potassium sulphocyanate with allyl iodide (v. 516), or with allyl bromide, or with the potassium salt of allyl-sulphuric acid. The product obtained by either of these processes is identical in every respect with natural oil of mustard (Tollens, *Zeitschr. f. Chem.* [2] v. 90).

Mustard-oil heated with *alcohol* a little above 100° unites with it, forming semi-sulphuretted allyl-urethane, $CS\left\{\begin{matrix}NH(C^3H^5)\\OC^2H^5\end{matrix}\right.$ (Hofmann, p. 1050). According to L. Henry (*Jahresb.* 1867, p. 379), it unites directly with dry *hydrobromic acid*, forming a crystalline compound, from which it is separated by water. With dry *hydriodic acid* it forms a pitchy mass. Heated in alcoholic solution with *zinc* and *hydrochloric acid*, it is converted into allylamine, hydrogen sulphide, and carbon dioxide:

$$N\left\{\begin{matrix}CS\\C^3H^5\end{matrix}\right. + 2H^2O = N\left\{\begin{matrix}C^3H^5\\H^2\end{matrix}\right. + H^2S + CO^2$$

(Oeser, *Ann. Ch. Pharm.* cxxxiv. 7).

The following normal sulphocyanic ethers have been prepared by L. Henry (*Deut. chem. Ges. Ber.* ii. 207; *Zeitschr. f. Chem.* [2] v. 206).

Benzyl Sulphocyanate, $C^7H^7.CNS$ or $S\left\{\begin{matrix}CN\\C^7H^7\end{matrix}\right.$, is produced by heating benzyl chloride with potassium cyanate in a water-bath, and crystallises from alcohol in large transparent prisms, insoluble in water, slightly soluble in cold alcohol, easily in hot alcohol, also in ether and in carbon bisulphide. It has a sharp smell and taste, melts at 36°–38°, and boils with partial decomposition at 256°. It unites readily with dry gaseous hydrogen bromide, forming a crystallised compound, insoluble in ether, immediately decomposed by water. Fuming nitric acid converts it into *nitrobenzyl sulphocyanate*, $C^7H^6(NO^2).CNS$, which is also produced from nitrobenzyl chloride, $C^7H^6(NO^2)Cl$, and potassium sulphocyanate, and crystallises from alcoholic solution in small brittle needles, volatilising at about 70°, and decomposing before it distils.

Glyceryl Sulphocyanate, $C^3H^5(CNS)^3$, is prepared by the action of potassium sulphocyanate in alcoholic solution at 100° on isotribromhydrin (produced by the action of bromine on allyl iodide); ordinary trichlorhydrin does not yield it. The compound separates from the alcoholic liquid in the crystalline form, and when recrystallised from alcohol forms small, white, shining, hard, brittle needles, having neither taste nor smell. It melts at 126°, and soon afterwards decomposes, giving off hydrogen cyanide and leaving a carbonaceous residue. It is quite insoluble in water, very slightly soluble in cold alcohol, much more soluble in boiling alcohol (Henry).

General Reactions of the Sulphocarbimides and Sulphocyanic Ethers.—The bodies of both these groups (taking the methyl-compounds for example) are ultimately produced from methyl-alcohol, carbon bisulphide, and ammonia, with elimination of 1 mol. water and 1 mol. hydrogen sulphide:

$$CH^4O + CS^2 + NH^3 = H^2O + H^2S + C^2H^3NS,$$

the nature of the resulting compound depending only on the order in which the reactions take place. In the case of methyl-sulphocarbimide we have:

$$(1)\ .\ .\ CH^4O + NH^3 = H^2O + N\left\{\begin{matrix}CH^3\\H^2\end{matrix}\right.$$

$$(2)\ .\ .\ N\left\{\begin{matrix}CH^3\\H^2\end{matrix}\right. + CS^2 = H^2S + N\left\{\begin{matrix}CS\\CH^3\end{matrix}\right.$$

and in that of methyl-sulphocyanate (see v. 504):

$$(1)\ .\ .\ NH^3 + CS^2 = H^2S + S\left\{\begin{matrix}CN\\H\end{matrix}\right.$$

$$(2)\ .\ .\ S\left\{\begin{matrix}CN\\H\end{matrix}\right. + CH^4O = H^2O + S\left\{\begin{matrix}CN\\CH^3\end{matrix}\right.$$

These considerations are supported by the following reactions: When an alcoholic solution of ethyl-sulphocarbimide is mixed with *zinc* and *hydrochloric acid*, hydrogen sulphide is given off for several days in continually decreasing quantity, but no carbon dioxide, whilst the liquid becomes filled with white needles of formic sulphaldehyde,

CH^2S; and on mixing the liquid filtered from these crystals with strong soda-ley the precipitated zinc oxide redissolves, and then adding alcohol, an oily layer of ethyl-amine and methyl-ethylamine rises to the surface. The principal reaction is:

$$N\left\{\begin{matrix}CS\\C^2H^5\end{matrix}\right. + 2HH = CH^2S + N\left\{\begin{matrix}C^2H^5\\H^2\end{matrix}\right.$$

and at the same time there is a secondary reaction, represented by the equation

$$N\left\{\begin{matrix}CS\\C^2H^5\end{matrix}\right. + 3HH = H^2S + N\left\{\begin{matrix}CH^3\\C^2H^5.\\H\end{matrix}\right.$$

When the isomeric compound, ethyl-sulphocyanate, is treated with zinc and hydrochloric acid, hydrogen sulphide is likewise evolved without carbon dioxide, but it is largely mixed with hydrogen cyanide, ethyl sulphydrate, ethyl sulphide, and marsh gas, and on distillation a certain quantity of ethyl bisulphide is likewise obtained. The residue heated with soda-ley yields ammonia and methylamine. In this case the principal decomposition is represented by the equation:

$$S\left\{\begin{matrix}CN\\C^2H^5\end{matrix}\right. + HH = CNH + S\left\{\begin{matrix}C^2H^5\\H\end{matrix}\right.$$

and the secondary reaction by

$$2S\left\{\begin{matrix}CN\\C^2H^5\end{matrix}\right. + 8HH = S\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right. + 2NH^3 + 2CH^4 + H^2S.$$

The hydrogen cyanide is partly converted into methylamine: $CNH + 2H^2 = N(CH^3)H^2$.

The action of nascent hydrogen on allyl-sulphocarbimide is analogous to that of ethyl-sulphocarbimide (contrary to the observations of Oeser, p. 1057), the principal products being formic sulphaldehyde and allylamine:

$$N\left\{\begin{matrix}CS\\C^3H^5\end{matrix}\right. + 2HH = CH^2S + N\left\{\begin{matrix}C^3H^5\\H^2\end{matrix}\right.$$

while hydrogen sulphide, allylamine (no methyl-allylamine), and marsh gas are obtained as secondary products:

$$N\left\{\begin{matrix}CS\\C^3H^5\end{matrix}\right. = 4HH = N\left\{\begin{matrix}C^3H^5\\H^2\end{matrix}\right. + CH^4 + H^2S.$$

In the action of nascent hydrogen on sulphocyanic acid (zinc, hydrochloric acid, and potassium sulphocyanate) the reaction goes on in both ways; thus:

$$N\left\{\begin{matrix}CS\\H\end{matrix}\right. + 2HH = CH^2S + NH^3$$

and

$$S\left\{\begin{matrix}CN\\H\end{matrix}\right. + HH = H^2S + CNH.$$

The hydrogen cyanide, however, appears only as methylamine.

Ethyl-sulphocarbimide heated with *water* in a sealed tube to 200° for several hours is resolved into ethylamine, carbon dioxide, and hydrogen sulphide:

$$N\left\{\begin{matrix}CS\\C^2H^5\end{matrix}\right. + H^2O = N\left\{\begin{matrix}C^2H^5\\H^2\end{matrix}\right. + CSO$$

and

$$CSO + H^2O = CO^2 + H^2S.$$

The same reaction takes place when concentrated hydrochloric acid is used instead of water, but it is then complete after an hour's heating to 100°. Ethyl sulphocyanate is but slowly decomposed by water even at high temperatures, considerable quantities remaining unaffected even after heating to 200° for several days. With strong hydrochloric acid, the decomposition is easier, the products being ethyl sulphide, ammonia, carbon dioxide, and hydrogen sulphide:

$$S\left\{\begin{matrix}CN\\C^2H^5\end{matrix}\right. + H^2O = S\left\{\begin{matrix}C^2H^5\\H\end{matrix}\right. + CNOH$$

$$CNOH + H^2O = NH^3 + CO^2$$

$$2S\left\{\begin{matrix}C^2H^5\\H\end{matrix}\right. = H^2S + S\left\{\begin{matrix}C^2H^5\\C^2H^5.\end{matrix}\right.$$

Allyl-sulphocarbimide is decomposed by water at high temperatures, especially in presence of hydrochloric acid, according to the equation:

$$N\left\{\begin{matrix}CS\\C^3H^5\end{matrix}\right. + 2H^2O + N\left\{\begin{matrix}C^3H^5\\H^2\end{matrix}\right. CO^2 + H^2S.$$

At the same time, however, another reaction takes place, whereby a second liquid base is formed, boiling at a very high temperature and forming an amorphous platinum salt.

On ethyl-sulphocarbimide, dilute *sulphuric acid* acts in the same manner as water and hydrochloric acid. With strong sulphuric acid, on the contrary, it mixes, producing great rise of temperature, and after a few minutes extremely rapid evolution of carbon oxysulphide; the residue contains ethylamine sulphate:

$$N\left\{\begin{matrix}CS\\C^2H^5\end{matrix}\right. + H^2O = CSO + N\left\{\begin{matrix}C^2H^5\\H^2.\end{matrix}\right.$$

In contact with water, and especially in presence of an alkali, the carbon oxysulphide is resolved into carbon dioxide and hydrogen sulphide.

Ethyl sulphocyanate is also but slowly acted upon by dilute sulphuric acid, rapidly by the concentrated acid, with considerable rise of temperature, and evolution of carbon dioxide and sulphur dioxide. On adding water and distilling, sulphuretted ethereal products pass over, and the brown residue heated with potash gives off considerable quantities of ammonia. The reaction appears therefore to be similar to that which takes place with water and hydrochloric acid, the sulphur being separated in connection with the ethyl group (Hofmann). Schmitt a. Glutz (*Zeitschr. f. Chem.* [2] iv. 723) by treating ethyl sulphocyanate with strong sulphuric acid, obtained carbonyl-disulphodiethyl, $CO\left\{\begin{matrix}SC^2H^5\\SC^2H^5,\end{matrix}\right.$ isomeric with xanthic ether, $CS\left\{\begin{matrix}SC^2H^5\\OC^2H^5,\end{matrix}\right.$ according to the equation:

$$2S\left\{\begin{matrix}CN\\C^2H^5\end{matrix}\right. + 3H^2O + 2H^2SO^4 = CO\left\{\begin{matrix}SC^2H^5\\SC^2H^5\end{matrix}\right. + CO^2 + 2(NH^4.HSO^4).$$

Methyl sulphocyanate and amyl sulphocyanate yield homologous compounds.

On allyl-sulphocarbimide, sulphuric acid acts in the same manner as on the ethyl compound:

$$N\left\{\begin{matrix}CS\\C^3H^5\end{matrix}\right. + H^2O = CSO + N\left\{\begin{matrix}C^3H^5\\H^2.\end{matrix}\right.$$

This reaction is well adapted for the preparation of allylamine.

Phenyl- and tolyl-sulphocarbimide, treated with sulphuric acid, yield carbon oxysulphide and the corresponding sulphuric acid: *e.g.*,

$$N\left\{\begin{matrix}CS\\C^6H^5\end{matrix}\right. + H^2SO^4 = CSO + NH(C^6H^5).SO^3H.$$

With *nitric acid*, ethyl-sulphocarbimide forms ethylamine, carbon dioxide, and sulphuric acid, whereas ethyl-sulphocyanate, as shown by Muspratt, yields ethyl-sulphurous acid, $C^2H^5SO^3H$. The homologous sulphocarbimides and allyl-sulphocarbimide act in the same manner.

Under the influence of sodium, ethyl sulphocyanate is completely resolved into cyanogen and ethyl bisulphide (Hofmann):

$$2S\left\{\begin{matrix}CN\\C^2H^5\end{matrix}\right. + Na^2 = 2CNNa + S^2(C^2H^5)^2.$$

SULPHOMETHYLIC ALDEHYDE. CH^2S.—Syn. with Formic Sulphaldehyde (p. 622).

SULPHONAPHTHALENE CHLORIDE. $C^{10}H^7SO^2Cl$.—Syn. with Naphthylsulphurous Chloride (p. 860).

SULPHONAPHTHALIC ACID. $C^{10}H^8SO^3$.—Syn. with Naphthylsulphurous Acid (p. 860).

SULPHOPHENOLIC ACID. $C^6H^6SO^4$.—Syn. with Phenylsulphuric Acid (p. 923).

SULPHOPHENYLENE-ETHYLENE. $C^8H^8SO^2 = C^6H^4SO^2.C^2H^4$ (Otto, *Ann. Ch. Pharm.* cxliii. 205).—This compound, originally observed by Kalle (*Jahresb.* 1861, p. 628) to be produced in the action of zinc-ethyl on phenylsulphurous chloride, and in the preparation of phenylsulphurous hydride by the action of sodium-amalgam on phenylsulphurous chloride (v. 564), may be prepared by treating the product of the action of sodium-amalgam on an ethereal solution of the chloride, after removal of the ether, with water and hydrochloric acid, washing the oil thereby separated with sodium carbonate, and dissolving it in ether, which leaves it behind on evaporation. It is an oily liquid, having a faint yellowish colour, and a peculiar unpleasant sweetish odour, heavier than water, and insoluble therein, miscible in all proportions with alcohol, ether, and benzol. In hot water it dissolves slightly, forming a liquid which becomes milky on cooling. When heated alone, it is resolved into carbon, sulphurous oxide, and an oil having an odour of radishes. It dissolves with violet-red colour in warm fuming sulphuric acid; does not unite with alkaline bisulphites. By zinc and sulphuric acid, it is resolved into phenyl-sulphydrate and alcohol:

$$C^6H^4SO^2.C^2H^4 + 6H = C^6H^6S + C^2H^6O + H^2O.$$

With fuming nitric acid it yields nitrophenylsulphurous acid, together with traces of nitrobenzene and picric acid.

SULPHOTOLUOLAMIDE, $C^7H^7.SO^2NH^2$, separates from a solution of sulphotoluolic bromide, $C^7H^7SO^2Br$, in concentrated aqueous ammonia, on evaporation, in large nacreous laminæ. It is moderately soluble in hot alcohol and water, and melts at 139°–140° (Otto a. von Grüber, *Ann. Ch. Pharm.* cxlii. 92; *Jahresb.* 1866, p. 6

SULPHOTOLUOLIC ACID. Syn. with TOLUENE-SULPHURIC or TOLUENE-SULPHUROUS ACID (p. 286).

SULPHOTOLYLENE-ETHYLENE. $C^9H^{12}SO^2 = C^7H^8SO^2 C^2H^4$ (Otto, *Ann. Ch. Pharm.* cxliii. 205).—This compound, obtained as a secondary product in the preparation of toluene-sulphurous acid, forms, after repeated crystallisation from dilute alcohol, small, shining, oblique, rhombic prisms, insoluble in water, slightly soluble in cold, easily in hot alcohol, ether, and benzol. It melts at 75°–76° and behaves in other respects like the corresponding phenylene-compound. With zinc and dilute sulphuric acid it yields alcohol and nitrobenzylsulphydrate, C^7H^8S, identical with that which is obtained from sulphotoluolic chloride or from toluene-sulphurous acid. With fuming nitric acid, it yields nitrotoluene-sulphuric acid, $C^7H^7(NO^2)SO^3$, together with secondary products. With bromine in ethereal solution it forms the compound $C^{18}H^{20}Br^2S^2O^4$, which crystallises from ethereal solution in long needles, melting at 95°, and converted by heating with absolute alcohol into ethyl toluene-sulphate, $C^7H^7SO^3.C^2H^5$. This ether is likewise formed by the action of bromine on an alcoholic solution of sulphotolylene-ethylene.

When sulphotolylene-ethylene, dissolved in pure amylic ether or in a mixture of amylic ether and toluene, is treated with sodium-amalgam, there is formed, not sulphotolylene-amylene, but—together with metabenzyl bisulphide and a mercury-compound which crystallises in needles—either a body, $C^{12}H^{16}S^2O^4$, melting at 35° to 36°, or a compound, $C^{12}H^{16}S^2O^5$, crystallising in four-sided prisms and melting at 78°–79°.

SULPHOXYBENZOIC ACID. See OXYBENZOIC ACID (p. 890).

SULPHUR. *Modifications.*—A soft, amorphous, yellow, opaque sulphur of sp. gr. 1·82–1·87, sparingly soluble in carbon bisulphide, is obtained, according to W. M (*Pogg. Ann.* cxxvii. 404; cxxxiii. 347), by passing dry hydrogen sulphide over heated oxalic acid, or by passing sulphur-vapour evolved in a stream of carbon dioxide or hydrochloric acid into water. It does not lose its softness by pressure, and is but slightly soluble in carbon bisulphide. According to Sestini (*Bull. Soc. Chim.* [2] v. 195), the supposed modification described by Müller is nothing but sulphur in the utricular form, which it assumes on rapid condensation in contact with the air. According to Berthelot, on the other hand (*ibid.* 197), sulphur condensed in water is identical with that which is condensed in the air, only while in the soft elastic state; when hardened it contains a different amount of insoluble sulphur. According to De Luca and Ubaldini (*Compt. rend.* lxiv. 1200), sulphur separated from aqueous sulphurous acid (with simultaneous formation of pentathionic acid) by the action of hydrogen sulphide, consists partly of the insoluble modification, the proportion varying with the duration of the contact and other conditions of the experiment. When the sulphurous acid is in excess the insoluble modification predominates.

Sulphur may be crystallised from fusion in the rhombic form (v. 530), by filling a long-necked flask, having a capacity of 150–200 centrimetres, with pure sulphur, drawing out the neck to a capillary orifice with two or three bends, melting the sulphur in an oil-bath at 120°, and then immersing the flask in water at 90°. The sulphur then remains liquid for a long time, and crystals gradually form, both on the surface and within the mass, and may be at least partially isolated by inverting the flask, so that the still fluid portion may run into the neck. These crystals are transparent, agree in form and in their angles with native sulphur, and may be kept without alteration. Their formation is facilitated by adding a few drops of carbon bisulphide to the sulphur before fusion.

The solubility of sulphur in *carbon bisulphide* and other liquids has been determined by Cossa:

Temperature	Sulphur in 100 pts. CS^2	Temperature	Sulphur in 100 pts. CS^2
—11°	16·54	22°	46·05
—6°	18·75	38°	94·57
0°	23·99	48·5°	146·21
+15°	37·15	55°	181·34
18·5°	41·65		

The dissolution is attended with absorption of heat: when 20 pts. sulphur are dissolved in 50 pts. of the bisulphide at 22°, the fall of temperature amounts to about 5°. The saturated solution boils at 55° (pure carbon bisulphide at 46·8°).

100 pts. benzene dissolve	0·965 pts. sulphur at	26°.
	4·377	„	71°.
100 pts. toluene „	1·479	„	23°.
100 pts. ethyl oxide „	0·972	„	23·5°.
100 pts. chloroform „	1·205	„	22°.
100 pts. phenol „	16·35	„	174°.
100 pts. aniline „	85·96	„	130°.

Coal-naphtha dissolves about 2 p. c. sulphur at ordinary temperatures, nearly half its weight at temperatures near the boiling point. The solvent power of coal-naphtha for sulphur increases with its specific gravity; certain heavy coal-tar oils dissolve as much as 115 p. c. sulphur at 110°, and an almost unlimited quantity at 120° (E. Pelouze, *Compt. rend.* lxviii. 1179; lxix. 56).

Reactions.—When a series of electric sparks is passed through a mixture of sulphur-vapour and *oxygen*, combination takes place, sometimes with slight explosion, and sulphurous oxide is produced. *Hydrogen* and sulphur unite easily under similar circumstances, forming H^2S. With *nitrogen* no reaction takes place. With *monoxide* and *dioxide of nitrogen*, sulphurous oxide and nitrogen are formed, and on passing the products into a dry glass vessel cooled with water, splendid leaden-chamber crystals are obtained. *Carbon monoxide* unites easily with sulphur, under the same circumstances, forming carbon oxysulphide; *carbon dioxide*, which is resolved by the electric spark into the monoxide and oxygen, yields carbon oxysulphide and sulphurous oxide (Chevrier, *Compt. rend.* lxix. 136).

When hydrogen gas is passed through boiling sulphur, hydrogen sulphide is abundantly produced. Sulphur likewise acts on boiling *aniline*, giving rise to rapid evolution of hydrogen sulphide and formation of a sulphuretted base. Other organic bodies, as acetanilide, glycerin, naphthalene, &c., are likewise attacked by sulphur (Merz a. Weith, *Zeitschr. f. Chem.* [2] v. 603).

Detection by the Spectroscope.—The flame of sulphur burning in the air gives a continuous spectrum; so likewise does that of hydrogen burning in oxygen. But when sulphur-vapour is passed into a hydrogen-flame, a very beautiful and complicated spectrum is formed, which was first observed by Mulder in 1864. This spectrum is not seen in the hot part of the flame, where the oxygen enters, but only in the inner part, consisting of nearly pure hydrogen heated to a comparatively low temperature; this part of the flame may also be distinguished with the naked eye, by its fine blue colour. On cooling the sulphuretted flame, the same colour appears at the cooled part. The spectrum of sulphur consists of a number of bright and nearly equidistant lines in the green and the blue. Towards the violet these lines unite in bands. When a flame of pure hydrogen burning from a platinum jet is directed over the surface of sulphuric acid, the cooled part of the flame acquires a splendid blue colour with a tinge of violet, and exhibits the spectrum above described, whence it may be inferred that the sulphur is separated in the free state in the reducing flame. On passing vapour of sulphuric or sulphurous acid into the flame, the axis becomes coloured in the same manner as in the experiment with sulphur-vapour. The same characteristic colour is observed when a hydrogen flame is directed upon a crystal of sodium sulphate, ammonium sulphate, alum, gypsum, &c., or of a sulphite or hyposulphite; with barium sulphate however it is not produced. The flame of hydrogen burning under a bell-jar frequently exhibits a blue colour at the edges, and the same blue tint is almost always observed when the flame of hydrogen is passed over the surface of a glass vessel. This blue flame exhibits the spectrum of sulphur, and the presence of that element in the flame is due to reduction of sulphates in the glass or to sulphuric acid in the air (Salet, *Compt. rend.* lxviii. 404; *Zeitschr. f. Chem.* [2] v. 223). W. F. Barret also has observed that when a pure hydrogen-flame is directed on the surface of various solid bodies, metallic or non-metallic, and on several liquids, a ring of deep [illegible] light is produced, due also to sulphur, derived from the air (*Phil. Mag.* [4] xxx. [illegible] *Jahresb.* 1865, p. 139). On the spectrum of sulphur see also SPECTRAL ANALYSIS (p. 1032); further, Salet (*Compt. rend.* lxxiii. 559), and Ditte (*ibid.* 622); also Chem. *Soc. J.* [2] ix. 1145, 1146.

On the estimation of sulphur in iron, see Eggertz (*Chem. News*, 1868, p. [illegible] in organic bodies, ANALYSIS, ORGANIC (p. 148).

Recovery of Sulphur from Alkali-waste (v. 529).—A historical notice of the several processes devised for this purpose has been given by A. Scheurer-Kestner (*Bull. Soc. industr. de Mulhouse*, février 1858; *Bull. Soc. Chim.* [2] ix. 419). The methods proposed down to the year 1855 had for their object to utilise these residues for the preparation of hyposulphites, or to evolve hydrogen sulphide from them, and [illegible] this to separate the sulphur or prepare sulphurous acid. The subsequent improvements relate: 1. To the oxidation of the residues by air in such a manner that the soluble oxidation-product may be decomposed by acids without evolution of gas, so that only one equivalent of acid may be required for the separation of several equivalents of sulphur.—2. The use of crude manganese solution (chlorine-residues) in place of hydrochloric acid.—3. The extraction of the pure fused sulphur.

The first problem has been solved by Guckelberger and by Schaffner. Guckelberger in 1858 began experiments, which were carried on from 1859 to 1861 under his direction by L. Mond, and had for their object to determine the duration of oxidation for the layers which would yield the maximum quantity of hyposulphites. The quantity of sulphur present in the form of hyposulphites was found to be as follows:

	After 14 days.	After 4 weeks.	After 6 weeks.	After 10 weeks.
For 100 pts. of the moist residue .	2·5	4·5	1·0	0·7
For 100 pts. of the dry residue . .	2·6	4·0	12·0	1·6

Guckelberger also found that the oxidation takes place more easily, and with [illegible] of heat, when the residues are exposed to the air in heaps of considerable size, and that then also the further rapid oxidation of the calcium sulphides may be avoided. In this manner (1862) he obtained solutions from which the sulphur was separated by acids without evolution of gas, but it was only in 1864 that he prepared the regenerated sulphur on the manufacturing scale. Patents for the oxidation of the residues were taken out by Mond in 1861 and 1863. His last process (1867) is as follows: The residues, without removal from the lixiviating tanks, are treated for [illegible] to 24 hours with a current of air driven by a ventilator till they assume a yellow-green colour, after which they are subjected to methodical lixiviation, and this treatment is repeated several times. The oxidation must be so regulated that the liquor may contain 2 mol. sulphide to 1 mol. hyposulphite (if it is carelessly conducted the hyposulphite is converted into sulphite and sulphydrate of calcium). The quantity of acid required to nearly saturate the lime (present as sulphide and hyposulphite) is then added, taking care to leave the liquid slightly alkaline, and the whole is heated to [illegible] by a current of steam. The nearly pure sulphur thus separated is washed and melted. The yield amounts to about $\frac{3}{5}$ of the total quantity of sulphur in the alkali-waste, the other $\frac{2}{5}$ being left behind as sulphite and sulphate of calcium. To determine the quantities of hyposulphite, &c., in the liquors:—1. The quantity of hyposulphite is titrated with iodine, after the sulphides and sulphydrates have been decomposed by excess of zinc-chloride.—2. A second sample is mixed with iodine and starch till a blue colour appears, and after decoloration with sodium hyposulphite it is neutralised with caustic soda. According to the equations $CaS^x + I^2 = CaI^2 + S^x$; CaH^2S^2 + $4I = CaI^2 + S^2 + 2HI$; $2HI + Na^2O = 2NaI + H^2O$, the second titration with iodine gives the total quantity of hyposulphite, sulphide, and sulphydrate; the titration with soda gives the amount of sulphydric acid (Mond, *Chem. News*, xv. 183; xvi. 27, 41; *Jahresb.* 1867, p. 901). See also Schaffner (*Zeitschr. f. Chem.* [2] v. [illegible] *Dingl. pol. J.* cxcii. 308; *Jahresb.* 1868, p. 925).

The use of crude manganese solution instead of hydrochloric acid was tried by Townshend and Walker in 1860, and afterwards successfully carried out by P. W. Hofmann (*Chem. News*, xvi. 163; *Jahresb.* 1866, p. 857); by E. Kopp (*Ann. Ch. Phys.* [4] vii. 5, 63; *Bull. Soc. Chim.* [2] 335, 440; *Chem. News*, xii. 264, 290; xiii. [illegible] 40, 111, 140; *Jahresb.* 1865, p. 779; further: *La dénaturation et utilisation des résidus de la fabrication de la soude et du chlorure de chaux*, Paris, 1868; also *Jahresb.* 1868, p. 923); see also P. W. Hofmann (*Chem. News*, xvi. 163; *Jahresb.* 1866, p. 857), and Rosenstiehl (*Bull. Soc. Chim.* [2] ix. 339; *Jahresb.* 1868, p. 923).

OXYGEN-COMPOUNDS OF SULPHUR.

1. **Hyposulphurous Acid.** $H^2SO^2 = \left.\begin{matrix}H\\H\end{matrix}\right\}SO^2$.—*Hydrosulphurous Acid* (Schützenberger, *Zeitschr. f. Chem.* [2] v. 546).—This acid is produced by the action of zinc on aqueous sulphurous acid. The metal dissolves without evolution of hydrogen, forming a yellow solution which possesses a decolorising power much greater than that of sulphurous acid itself, throws down from cupric sulphate a precipitate of copper hydride, Cu^2H^2, mixed, if the copper solution is in excess, with metallic copper, and immediately reduces the metals from silver and mercury salts. The solution thus obtained is, however, very unstable; its decolorising power attains a maximum in a few minutes, then diminishes, while at the same time it loses its yellow colour and becomes milky from separation of sulphur; it then contains thiosulphuric acid, $H^2S^2O^3$.

A more definite product is obtained by immersing clippings of zinc in a concentrated solution of acid sodium sulphite contained in a closed vessel. The zinc then dissolves as before without evolution of hydrogen, the reaction being completed in about half an hour, and an abundant crystallisation of zinc-sodium sulphite is produced. The decanted liquid, which possesses very great decolorising power, becomes very hot on exposure to the air, losing at the same time its characteristic properties, and afterwards containing nothing but the double salt just mentioned, together with acid sodium sulphite. To isolate a definite compound, the solution (about half a litre) is poured into a flask holding about two litres, and three-fourths filled with strong alcohol, and the flask is hermetically sealed. A crystalline precipitate is then immediately formed, consisting for the most part of zinc-sodium sulphite, while nearly all the bleaching compound remains dissolved in the alcohol. This solution decanted into a flask quite filled with it, well closed, and left to stand in a cool place, solidifies in a few hours to a mass of slender colourless needles, which must be pressed as quickly as possible between folds of linen, and dried in a vacuum, as it becomes very hot if exposed to the air in the moist state; when dry, however, it is not affected by oxygen. This salt contains but a small quantity of zinc, from which it may be freed by solution in water and reprecipitation with alcohol. It then consists of *sodium hyposulphite*, $NaHSO^2$. It is very soluble in water, soluble also in dilute alcohol, insoluble in strong alcohol. Its solution possesses all the decolorising and reducing powers above mentioned. The crystals when exposed to the air are completely converted into acid sodium sulphite, $NaHSO^3$, without formation of other products. When heated in a tube, they give off sulphur and sulphurous acid, together with a little water, and leave a residue of sodium sulphate and sulphide.

Hyposulphurous acid, which is much more unstable than its sodium salt, may be separated therefrom by treating the crystals with oxalic acid. A deep orange-yellow solution is then formed, possessing great decolorising power, and quickly becoming colourless, with deposition of sulphur. The formation of the acid by the action of zinc on sulphurous acid is represented by the equation:

$$H^2SO^3 + Zn = ZnO + H^2SO^2.$$

The same reaction takes place with other metals, as iron or manganese. The formation of thiosulphates in all these cases is only a secondary reaction due to the slow and spontaneous decomposition of the hyposulphite.

When a porous earthenware cell filled with acid sodium sulphite is immersed in weak sulphuric acid, and the liquid subjected to electrolysis, the negative pole dipping into the acid sulphite, oxygen is evolved at the positive pole, while at the negative pole no gas is evolved, but the sulphite is converted into hyposulphite. By replacing the nitric acid in a Bunsen's cell with acid sodium sulphite, a combination is obtained, which is very little inferior in intensity to the ordinary Bunsen's battery, and remains constant for a considerable time (Schützenberger).

Ethyl-hyposulphurous Acid. $C^2H^6SO^2 = \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}SO^2$ (Wischin, *Ann. Ch. Pharm.* cxxxix. 364).—This acid, called by its discoverer *ethyl-sulphurous acid*, is produced as a zinc-salt by the action of zinc-ethyl on sulphuric anhydride, $2SO^3 + Zn(C^2H^5)^2 = SO^2 + ZnSO^4 + C^4H^{10}$; and $2SO^2 + Zn(C^2H^5)^2 = Zn(C^2H^5SO^2)^2$. When zinc-ethyl is carefully mixed with an equivalent quantity of sulphuric anhydride in a strong tube sealed and filled with dry carbon dioxide, a violent reaction takes place, very apt to give rise to explosion, and zinc ethyl-hyposulphite is formed, together with combustible gases, sulphurous anhydride, zinc sulphate, zinc sulphide, and metallic zinc. Ethyl-hyposulphurous acid is also formed (contrary to the separates in colourless needles, insoluble in water, slightly soluble in cold alcohol and ether, more easily in boiling alcohol. It sublimes without decomposition in long needles, melts at 235°, and is very stable, not being attacked by weak oxidising agents, or by cold potash-ley. Boiling potash slowly converts it into chloranilate and acetate of potassium. Koch's hydrochloranilic chloride is regarded by Graebe as a tetrachlorinated substitution-product of pyrocatechin or resorcin.

Tetrachlorotetroxyquinhydrone, $C^{12}Cl^4H^6O^8$, is formed by the incomplete reduction of chloranilic acid by sulphurous acid, or when hydrochloranilic acid is oxidised by exposure to the air. It crystallises in slender black needles; is converted by oxidation into chloranilic acid, and by further treatment with sulphurous acid into hydrochloranilic acid (Graebe).

Sulpho-acids derived from the Chlorinated Quinones and Hydroquinones.

The salt described by Hesse (v. 22) as potassium disulphodichlorosalicylate is, according to Graebe's analysis, the potassium salt of *dichlorhydroquinone-disulphuric acid*, $C^6Cl^2S^2H^2K^2O^8$. It is produced by adding tetrachloroquinone to a warm dilute solution of acid potassium sulphite:

$$C^6Cl^4O^2 + 3H(SO^3K) = C^6\left\{\begin{matrix}(OH)^2\\ Cl^2\\ (SO^3K)^2\end{matrix}\right. + 2HCl + KHSO^4.$$

Thiochronic Acid. $C^6H^6S^5O^{17}$.—The potassium salt of this acid, which Hesse obtained by the action of acid potassium sulphite on tetrachloroquinone, is conveniently prepared, according to Graebe, by saturating a slightly warmed dilute solution of neutral potassium sulphite with tetrachloroquinone, separating the yellow crystals which are deposited on cooling, from the lighter white crystals of the preceding salt formed at the same time, finally recrystallising it from water, and boiling it with alcohol to remove the last portions of the white salt. The air-dried thiochronate has the composition $C^6HS^5K^5O^{17} + 4H^2O$, and gives off 3 mol. water, at 130°. In its formation, the chlorine of the tetrachloroquinone is replaced by the group SO^3K, and the resulting compound, $C^6\left\{\begin{matrix}O^2\\ (SO^3K)^4\end{matrix}\right.$, unites with 1 mol. acid potassium sulphite, forming the thiochronate, $C^6\left\{\begin{matrix}OH\\ O(SO^3K)\\ (SO^3K)^4\end{matrix}\right.$. Heated with water in a sealed tube, it is resolved into *hydroquinone-disulphate* and acid sulphate of potassium, according to the equation:

$$C^6\left\{\begin{matrix}OH\\ O(SO^3K)\\ (SO^3K)^4\end{matrix}\right. + 3H^2O = C^6\left\{\begin{matrix}(OH)^2\\ H^2\\ (SO^3K)^2\end{matrix}\right. + 3KHSO^4.$$

The crystallised salt undergoes the same decomposition when quickly heated to 100°, and in dilute hydrochloric solution even at 100°. The hydroquinone-disulphate is also produced from the thiochronate, together with acid sulphite, by the action of reducing agents, as by boiling the solution with zinc-dust, or treating it with sodium-amalgam and hydrochloric acid. The attempt to prepare other salts of thiochronic acid was not successful.

Euthiochronic acid, produced by the action of alkalis on thiochronic acid, and regarded by Hesse (*Ann. Ch. Pharm.* cxiv. 292) as $C^5H^4S^2O^8$, by Greiff (*Jahresb.* 1863, p. 392) as $C^6H^6S^2O^{10}$, is, according to Graebe, *dioxyquinone-disulphuric acid*, $C^6H^4S^2O^{10} = C^6\left\{\begin{matrix}O^2\\ (OH)^2\\ (SO^3H)^2\end{matrix}\right.$. The formation of the potassium salt by the action of potash on the thiochronate, or on the dichlorhydroquinone-disulphate (in the latter case with aid of atmospheric oxygen), is represented by the following equations:

$$\underset{\text{Thiochronate.}}{\left\{\begin{matrix}OH\\ O(SO^3K)\\ (SO^3K)^4\end{matrix}\right.} + 2KOH = \underset{\text{Euthiochronate.}}{C^6\left\{\begin{matrix}(O^2)''\\ (OK)^2\\ (SO^3K)^2\end{matrix}\right.} + \underset{\text{Acid sulphite.}}{3KHSO^3}$$

$$\underset{\text{Dichlorhydroquinone-disulphate.}}{C^6\left\{\begin{matrix}(OH)^2\\ Cl^2\\ (SO^3K)^2\end{matrix}\right.} + 2KOH + O = \underset{\text{Euthiochronate.}}{C^6\left\{\begin{matrix}(O^2)''\\ (OK)^2\\ (SO^3K)^2\end{matrix}\right.} + 2HCl + H^2O.$$

Sulphurous acid in aqueous solution is reduced by *zinc* to hyposulphurous acid, SH^2O^2, the sulphur-analogue of formic acid (Schützenberger, p. 1063).

Sulphurous acid acts upon *stannous chloride* according to the following equations:

$$4SnCl^2 + 4HCl + SO^2 = 3SnCl^4 + SnS + 2H^2O$$
$$6SnCl^2 + 8HCl + 2SO^2 = 5SnCl^4 + SnS^2 + 4H^2O.$$

Moreover, on adding a cupric solution to a mixture of sulphurous acid with a large excess of stannous chloride, a black-brown precipitate is formed. Sulphurous acid reacts in the same manner with stannous chloride in presence of nearly all metals that are precipitable by hydrogen sulphide. Thus on passing gaseous sulphurous oxide through the hydrochloric acid solution of stannous chloride and *antimonious chloride* at ordinary temperatures, a yellow precipitate is formed which gradually turns red. At about 70° the reaction is quicker, and a dark red precipitate is immediately formed, free from tin, and consisting of a mixture of antimonious oxide and sulphide:

$$9SCl^2 + 2SbCl^3 + 3SO^2 + 12HCl = Sb^2S^3 + 9SnCl^4 + 6H^2O.$$

In like manner, sulphurous acid throws down from mixtures of stannous chloride with *platinic chloride*, *arsenious acid*, *copper salts*, or *bismuth salts*, the sulphides of platinum, arsenic, copper, or bismuth, the whole of the tin remaining in solution as stannic chloride. From a mixture of stannous chloride and *cadmium sulphate* the whole of the tin is precipitated as stannic sulphide, and from a mixture of stannous chloride and *lead acetate*, sulphurous acid throws down sometimes a tin sulphide, sometimes a yellow precipitate, which blackens with potash and consists of sulphide and chloride of lead (Federow, *Zeitschr. f. Chem.* [2] v. 15).

Sulphurous Chloride or *Thionyl Chloride*, $SOCl^2$, which Schiff obtained by the action of phosphorus pentachloride on sulphurous acid (v. 542), is also produced by the action of hypochlorous anhydride upon sulphur chloride, SCl^2, cooled to 10°, which contains sulphur in suspension. Separated by distillation from the sulphur chloride (which boils at 139°), it is a colourless, pungent liquid, having a sp. gr. of 1·675 at 0°, and boiling at 78° (Wurtz, *Compt. rend.* lxii. 460).

METALLIC SULPHITES.—*Ammonio-cuprous sulphite*, $(Cu^2)''(NH^4)^2(SO^3)^2 + 2H^2O$, is obtained in six-sided colourless plates by passing sulphurous oxide into an ammoniacal solution of cupric sulphate, or by digesting ammoniacal cupric acetate with metallic copper till it is decolorised, and then saturating with sulphurous acid. The *sodio-cuprous salt*, $(Cu^2)''Na^2(SO^3)^2 + 2H^2O$, is produced by adding sodium sulphite to concentrated cupric acetate till a permanent precipitate is formed; the liquid when left at rest deposits the double salt in colourless microscopic crystals mixed with an orange-yellow compound. By prolonged contact with the mother-liquor these crystals change into microscopic quadratic tablets, apparently consisting of $Cu^2Na^2(SO^3)^2 + 11H^2O$ (Commaille, *J. Pharm.* [4] vi. 107).

Gold Sulphites.—A double salt approximating in composition to the formula $(NH^4)^2SO^3.3(NH^3Au)^2SO^3 + 3H^2O$ is formed by gradually adding a nearly neutral solution of auric chloride to a gently warmed solution of 'ammon sulphite' (? sulphimic acid, NH^3SO^2) in strong ammonia. A precipitate of fulminating gold is formed at first, which afterwards dissolves, and the solution after some time deposits the double salt in six-sided laminæ. The mother-liquor contains an ammonio-aurous sulphite. When acid sodium sulphite is added by small portions to a strongly alkaline and nearly boiling solution of sodium aurate, a yellow precipitate is formed, which disappears on further addition of ammonium sulphite, the solution then containing a sodio-aurous sulphite analogous to the potassio-aurous salt described by Frémy (v. 545). A drop of the solution left to evaporate under the microscope leaves the double salt in purple-red crystals, but it cannot be purified by recrystallisation. The solution yields with barium chloride, first a white precipitate of barium sulphite and sulphate, and afterwards a purple-red precipitate of *bario-aurous sulphite*, $Au^2SO^3.3BaSO^3 + xH^2O$. From this barium salt the corresponding potassium and sodium salts may be obtained by double decomposition with alkaline carbonates. The *sodium salt* contains $Au^2SO^3.3Na^2SO^3 + 3H^2O$. The solution of this salt gives white precipitates with lead and silver salts, no precipitate with salts of calcium, strontium, magnesium, aluminium, zinc, copper, cobalt, or nickel (A. Haase, *Zeitschr. f. Chem.* [2] v. 535).

Platinum Sulphites.—*Double platinum sulphites* are obtained by passing sulphurous oxide into water in which platinic hydrate is suspended, till the hydrate begins to dissolve rapidly, mixing the filtered solution with an alkaline sulphite, and then with the corresponding carbonate in sufficient quantity to produce an alkaline reaction. The double salts then separate as red-brown crystalline precipitates. The *potassium salt*,

$K^2SO^3.(PtO)''SO^3 + H^2O$ or $\left.\begin{matrix}2(SO)'' \\ (PtO)'' \\ K^2\end{matrix}\right\}O^4 + H^2O$, is somewhat soluble in water, and separates from the solution by slow evaporation in the pulverulent form; the greater part however is reduced and crystallises out as potassio-platinous sulphite. The *sodium salt*, $2Na^2SO^3.(PtO)''SO^3 + 2H^2O$ or $3(SO)''.Na^4(PtO)''.O^6 + 2H^2O$, is [illegible] crystalline, and somewhat lighter in colour than the potassium salt. The [illegible] soluble *ammonio-platinum salt* is decomposed by evaporation, leaving the platinous double salt. All these platinum double sulphites are decomposed by hydrochloric acid, with formation of platinous and platinic chloride. Their solutions are reduced by hydrogen sulphide, but the platinum is not precipitated by hydrogen sulphide or ammonium sulphide except on addition of hydrochloric acid. With barium chloride they form a yellow precipitate soluble in acids, and containing all the platinum (Birnbaum, *Ann. Ch. Pharm.* cxxxix. 164; *Jahresb.* 1866, p. 269).

Potassio-platinous sulphite, $3K^2SO^3.Pt''SO^3 + 2H^2O = \left.\begin{matrix}(S''O)^4 \\ K^6Pt''\end{matrix}\right\}O^8 + 2H^2O$, is obtained by passing sulphurous oxide in excess through a solution of potassium sulphite in which platinic hydrate is suspended. The colourless solution yields the double salt on evaporation in stellate groups of needles moderately soluble in water. The [illegible] added to sodium salts throws down the sodio-platinous sulphite described by [illegible] Schnedermann (v. 549), the amount of water in which was found by Birnbaum correspond to the formula $3Na^2SO^3.PtSO^3 + 3H^2O$. The *ammonium salt*, $3(NH^4)^2SO^3.PtSO^3 + 3H^2O$, is prepared like the potassium salt, which it resembles in form and solubility; it is precipitated from its aqueous solution by alcohol, and afterwards dissolves but slowly in water. Its hydrochloric acid solution mixed with [illegible] and ammonia yields a precipitate of the salt described by Liebig (*Gmelin's Handb.* vi. 298), with an amount of water corresponding to the formula $(NH^4)^2SO^3.Pt$[illegible] H^2O. The aqueous solutions of all these salts give with barium chloride a [illegible] precipitate soluble in hydrochloric acid, and containing the whole of the platinum (Birnbaum, *loc. cit.*).

Platinosochlorosulphurous Acid. $Pt''\left\{\begin{matrix}Cl \\ SO^3H\end{matrix}\right.$.—This compound is obtained, in combination with sal-ammoniac, by adding ammonium platinochloride to concentrated aqueous sulphurous acid, warming the mixture on the water-bath, and replacing the sulphurous acid as it evaporates. On evaporating the resulting solution to the crystallising point, again mixing it with a slight excess of sulphurous acid, and leaving it to evaporate over oil of vitriol and quick lime, a few crystals of ammonium platinosochloride, $2NH^4Cl.PtCl^2$, first separate, and then long orange-yellow needles of the compound $Pt\left\{\begin{matrix}Cl \\ SO^3H\end{matrix}\right..2NH^4Cl$. By neutralising the solution with potassium carbonate, the corresponding potassium salt, $Pt\left\{\begin{matrix}Cl \\ SO^3K\end{matrix}\right..2NH^4Cl$, is obtained in well-defined rhombic crystals. The formation of the chloroplatinosulphurous acid is represented by the equation:

$$PtCl^2 + H^2SO^3 = HCl + Pt\left\{\begin{matrix}Cl \\ SO^3H\end{matrix}\right..$$

The compound $PtClSO^3H.2NH^4Cl$ is likewise formed, and even with greater facility, by directly dissolving ammonium platinosochloride in aqueous sulphurous acid. In like manner, by dissolving the same salt in a concentrated solution of neutral ammonium sulphite, a compound of ammonium platinosochlorosulphite with ammonium sulphite, $Pt\left\{\begin{matrix}Cl \\ SO^3NH^4\end{matrix}\right..(NH^4)^2SO^3 + 3H^2O$, is obtained in light yellow crystals apparently belonging to the monoclinic system. When potassium platinochloride is treated with excess of sulphurous acid, the yellow solution first deposits crystals of potassium sulphate; and on mixing the remaining liquid, which does not of itself yield any crystallisable compound, with potassium chloride, well-defined rhombic crystals are obtained, consisting of the salt $Pt\left\{\begin{matrix}Cl \\ SO^3K\end{matrix}\right..2KCl$. Lastly, by treating ammonium platinosochloride, $2NH^4Cl.PtCl^2$, with acid ammonium sulphite, both atoms of chlorine in the platinous chloride may be replaced by the univalent residue SO^3H, and the compound $Pt\left\{\begin{matrix}SO^3H \\ SO^3H\end{matrix}\right..2NH^4Cl + H^2O$ is obtained in large colourless crystals, which give off their water at 100°, and half their sulphurous acid as H^2SO^3 at 150°. The compound $Pt(SO^3H)^2$ is doubtless a bibasic acid, but its salts have not yet been examined (Birnbaum, *Zeitschr. f. Chem.* [2] v. 504).

Uranic Double Sulphites are obtained by passing sulphurous oxide into water in which uranic hydrate is suspended till a clear solution is obtained; concentrating this solution (which deposits uranic sulphite when heated), and mixing the filtrate with a strongly acid solution of potassium, sodium, or ammonium sulphite. The double salts then separate for the most part, and completely at a gentle heat, as yellow crystalline precipitates, which must be quickly collected on a filter, pressed, and dried over sulphuric acid and quick lime. When thus dried, they contain 1 or 2 mol. water, which they do not give up below the temperature at which they decompose. In the hypothetically anhydrous state they have the composition U^2MHSO^6 or $\left.\begin{matrix} SO'' \\ (U^2O^2)'' \\ HM \end{matrix}\right\}O^3$ [$M = K$, Na, or NH^4]. The sodium salt is the only one that is moderately soluble in water; in aqueous sulphurous acid they dissolve more freely, the sodium salt being the most, and the potassium salt the least soluble. The precipitate, commonly regarded as uranic sulphite, which is thrown down from uranic salts by ammonium sulphite at the boiling heat, appears to consist of ammonio-uranic sulphite (Scheller, *Ann. Ch. Pharm.* cxliv. 238).

Ethylsulphurous and ***Etherosulphurous Acids.*** $C^2H^6SO^3$.—Ethylsulphurous acid is the acid produced by oxidising mercaptan or ethyl sulphocyanate with nitric acid (v. 553); etherosulphurous acid by the action of potash-ley on neutral ethyl sulphite at a low temperature. The constitution of these two acids and their derivation from sulphurous acid are represented by Wurtz (*Ann. Ch. Phys.* [4] xii. 494) as follows:

$$HO—\overset{\prime\prime}{S}—O—OH$$
Sulphurous acid.

$$C^2H^5O—\overset{\prime\prime}{S}—O—OC^2H^5$$
Ethyl sulphite.

$$C^2H^5O—\overset{\prime\prime}{S}—O—OH$$
Ethylsulphurous acid.

$$HO—\overset{\prime\prime}{S}—O—OC^2H^5$$
Etherosulphurous acid.

To prepare etherosulphurous acid, Warlitz (*Ann. Ch. Pharm.* cxliii. 72) adds potassium hydrate dissolved in 5 pts. of water, in successive quantities, to an equivalent quantity of neutral ethyl sulphite; leaves the mixture to itself for several days till the supernatant layer of ethyl sulphite has disappeared; then saturates the liquid with carbonic acid; evaporates it to dryness in a vacuum; and treats the residue while warm with alcohol of 90 p. c. The potassium salt of etherosulphurous acid which remains after evaporating the alcoholic solution is pure after recrystallisation from absolute alcohol. It dissolves easily in water and in hot alcohol of 90 p. c., rather slowly in boiling absolute alcohol, and crystallises therefrom in soft scales having a satiny lustre. When recently prepared it is inodorous, but after some time it gives off the odour of ethyl sulphide, and the aqueous solution then contains a sulphate. When heated it carbonises more easily than the isomeric potassium ethylsulphite, giving off vapours of volatile sulphur-compounds having a peculiar odour. Heated with strong sulphuric acid, it decomposes at a temperature at which the ethyl sulphite remains unaltered, depositing drops of oil and emitting the odour of mercaptan. The vapours turn iodised starch-paper blue. Mixed with potassium cyanide it gives off the odour of ethyl cyanide, which is not the case with the ethyl sulphite (Warlitz).

According to Graebe (*Ann. Ch. Pharm.* cxlvi. 37), the potassium salt of ethylsulphurous acid is produced by the action of ethyl iodide on potassium sulphite. This reaction—which is general with the chlorides and iodides of the alcohol-radicles—is represented by the equation:

$$C^2H^5I + K^2SO^3 = KI + C^2H^5SO^3K.$$

3. Sulphuric Compounds.

SULPHURIC ACID and ANHYDRIDE. Sulphuric anhydride heated to 100° with *carbon tetrachloride* forms pyrosulphuric chloride, $S^2O^5Cl^2$ (p. 1070). With *chloroform* it reacts at ordinary temperatures, yielding carbon monoxide, pyrosulphuric chloride, and sulphuric chlorhydrate; similarly with bromine. When sulphuric anhydride and carbon bisulphide in nearly equivalent quantities are heated together on the water-bath, gas is given off, which, when freed from sulphurous anhydride and carbon bisulphide, consists of carbon oxysulphide (p. 406); the residue consists of pure sulphur (Armstrong, *Deut. chem. Ges. Ber.* ii. 712; *Zeitschr. f. Chem.* [2] vi. 247).

The compound $2SO^3.N^2O^3$ (v. 570) is formed directly by passing a series of induction-sparks through a dry mixture of oxygen, nitrogen, and sulphurous oxide, and collects on the sides of the vessel as a snowy crystalline mass (Marren, *Ann. Ch. Phys.* [4] iv. 300); also by passing a mixture of sulphurous oxide and nitrogen tetroxide through a strongly heated glass tube, or by passing sulphurous oxide over strongly heated lead nitrate (Weber, *Pogg. Ann.* cxxvii. 543).

The formation of sulphuric acid in the ordinary leaden-chamber process is effected, according to Weber, chiefly by the oxidising action of nitrous acid (produced by oxidation of nitrogen dioxide or by decomposition of the tetroxide). Pure nitric acid does not oxidise sulphurous acid, excepting in presence of a considerable quantity of sulphuric acid (Weber, *loc. cit.*; also *Jahresb.* 1866, p. 127).

Vertraet (*Dingl. pol. J.* clxxix. 63) proposes to replace the leaden chambers by a series of bottomless stone-ware vessels filled with coke and placed one above the other. Tardani a. Susini (*Bull. Soc. Chim.* [2] viii. 295) have patented a process in which the burning of the sulphur and the oxidation of the sulphurous acid take place in condensed air, and small leaden chambers are used having a capacity of about 3 cubic metres.

Sprengel (*Chem. Soc. J.* [2] iv. 455) has invented an apparatus, consisting of a graduated glass tube with a caoutchouc piston, for gauging the depth of liquid on the floor of the leaden chambers, and for withdrawing a sample of all the heterogeneous layers of liquid for determining the mean specific gravity.

The presence of sulphurous acid and of the lower oxides of nitrogen in ordinary sulphuric acid may be detected by half-filling a stoppered flask with it, and introducing into the upper part of the vessel a strip of paper impregnated with iodine and starch, which will be bleached if sulphurous acid is present, or a strip impregnated with potassium iodide and starch, which will be turned blue if the liquid contains any of the lower oxides of nitrogen. Both these impurities may be detected together, unless the sulphurous acid is in great excess (R. Warington, *Chem. News*, xvii. 75).

The heat-capacities of sulphuric acid and its hydrates have been found by L. Pfaundler (*J. pr. Chem.* ci. 507) to be as follows:

				Heat-capacity
SH^2O^4	between	77°	and 13°	0·3413
„	„	98°	„ 16°	0·3542
„	„	137°	„ 15°	0·3740
$SH^2O^4.H^2O$	„	75°	„ 14°	0·4478
„	„	98°	„ 18°	0·4527
$RH^2O^4.2H^2O$	„	70°	„ 14°	0·4703
„	„	98°	„ 16°	0·4703

Hence it appears: 1. That the heat-capacity increases with the proportion of water and with the temperature.—2. That the change of capacity with the temperature is greatest in pure hydrogen sulphate, and diminishes very quickly in the hydrates.

Marignac showed some years ago (*Ann. Ch. Phys.* [3] xxxix. 184) that sulphuric acid of any strength ($H^2SO^4 + xH^2O$ as well as $H^2SO^4 + xSO^3$) leaves when boiled down, not pure hydrogen sulphate, H^2SO^4, but a liquid having the composition $H^2SO^4.\frac{1}{12}H^2O$ or $SO^3.1\frac{1}{12}H^2O$; and that the only way of obtaining the pure compound H^2SO^4—besides direct combination of SO^3 and H^2O—is to expose oil of vitriol having as nearly as possible this composition to a very low temperature, whereupon the pure compound H^2SO^4 separates in crystals, the small excess of SO^3 or H^2O remaining in the mother-liquor. The crystals melt at 10·5°, the liquid heated to 30°–40° gives off vapours of SO^3, and when boiled is soon reduced to $H^2SO^4.\frac{1}{12}H^2O$.

In accordance with these results, it has been lately shown by Dittmar (*Chem. Soc. J.* [2] vii. 446) that when sulphuric acid, containing 99·5 p. c. of H^2SO^4 (prepared by mixing pure distilled oil of vitriol with the anhydride), is distilled under various pressures ranging from 3 to 314 centimetres of mercury, the residues are almost identical in composition with Marignac's hydrate, $H^2SO^4.\frac{1}{12}H^2O$; in other words, sulphuric acid, when boiled down under any pressure between these limits, behaves almost like a mixture of this stable hydrate with sulphuric anhydride. To account for this phenomenon, it is not, however, necessary to assume the existence of a stable molecule having the composition $12SO^3.13H^2O$. It is known that hydrogen sulphate, H^2SO^4, in the state of vapour, consists chiefly, and above certain temperatures entirely, of isolated molecules of SO^3 and H^2O (ii. 817). Now it may be assumed that in liquid sulphuric acid, even at low temperatures, some of the molecules have already assumed the state of motion corresponding to a temperature beyond that of dissociation (i. 866; iii. 133). The higher the temperature, the greater will be the ratio of the number of the dissociated molecules to that of the unchanged ones. The liberated molecules of H^2O and SO^3, being formed in the midst of a mass of molecules of H^2SO^4, will probably mostly unite with comparatively cold molecules of H^2SO^4, forming compounds represented by $H^2SO^4.xH^2O$ and $H^2SO^4.xSO^3$ respectively. Assuming now that the latter compounds are less stable than the former, it is easy to understand that in the distillation of sulphuric acid, the anhydride SO^3 (compared with $SO^3.H^2O$) will predominate in the vapour, and in a greater degree, the higher the temperature, *i.e.* the greater the pressure under which the liquid boils (Dittmar). See also Pfaundler (*Zeitschr. f. Chem.* [2] vi. 66).

Sulphuric Chorhydrate. $HClSO^3 = SO^2\begin{cases}Cl\\OH\end{cases}$.—Williamson obtained this compound by distilling strong sulphuric acid with phosphorus pentachloride (v. 576). According to S. Williams (*Chem. Soc. J.* [2] vii. 304), if an excess of sulphuric acid is used in this process, only a small quantity of the chlorhydrate is obtained. As soon as this is distilled off, sulphuric anhydride passes over, and afterwards, at a higher temperature, tabular crystals collect in the neck of the retort, probably consisting of a definite hydrate of sulphuric acid. Afterwards sulphuric acid distils over, and metaphosphoric acid remains behind. In neither of these distillates was phosphoric acid found after addition of water. Hence it follows that the phosphorus oxychloride formed in the first instance (v. 576) acts further on the sulphuric acid in a manner which may be represented by the equations:

$$POCl^3 + H^2SO^4 = PO^2Cl + HCl + HClSO^3$$

and

$$PO^2Cl + H^2SO^4 = HPO^3 + HClSO^3.$$

The greatest amount of sulphuric chlorhydrate is obtained when 3 mol. sulphuric acid are used to 1 mol. of the pentachloride, so as to ensure complete decomposition of the oxychloride. In this case the entire reaction is:

$$3H^2SO^4 + PCl^5 = 2HCl + PHO^3 + 3HClSO^3.$$

If a very large excess of sulphuric acid is used, no sulphuric chlorhydrate is obtained, but hydrochloric acid in large quantity, and sulphuric anhydride, because Nordhausen sulphuric acid is formed by the action of the chlorhydrate on the sulphuric acid:

$$HClSO^3 + H^2SO^4 = HCl + H^2SO^4.SO^3.$$

The vapour-density of the chlorhydrate, referred to hydrogen, was found by Dumas' method at 216° to be 32·857, which corresponds to a condensation to 3½ volumes. Hence it appears probable that the compound when vaporised is resolved into HCl and SO^3.

Dewar a. Cranston (*Chem. News*, xx. 174) prepare sulphuric chlorhydrate by the direct action of hydrochloric acid gas on sulphuric acid containing a large quantity of anhydride in solution; the action is very rapid and the temperature rises to 120°. The chlorhydrate heated to 100° in a sealed tube with *carbon bisulphide*, forms carbon oxysulphide, hydrochloric acid, and sulphurous anhydride:

$$CS^2 + HClSO^3 = HCl + SO^2 + CSO.$$

Sulphuric chlorhydrate acts violently on many organic compounds. With 1 mol. *ethyl alcohol* it forms a black tarry mass, which becomes very hot in contact with water, and gives off a gas which attacks the mucous membranes. With 2 mol. alcohol, the residue is a thickish liquid, from which water dissolves ethyl-sulphuric acid and separates oily neutral ethyl sulphate. With pure *ethyl oxide*, it likewise forms neutral ethyl sulphate. Heated to 140° with 1½ mol. *acetic acid*, it forms glycolsulphurous acid, $C^2H^4SO^5$. With *butyric acid* it yields disulphopropiolic acid, $C^3H^8S^2O^6$. One mol. *acetic anhydride* and 2 mol. sulphuric chlorhydrate, heated to 160° in a stream of carbon dioxide, yield an acid, $C^2H^6SO^7$, which, when separated from its lead salt and evaporated in a vacuum, remains as a deliquescent crystalline mass insoluble in alcohol and ether. The lead salt, $C^2H^4PbSO^7$, crystallises in white prisms (Baumstark, *Ann. Ch. Pharm.* cxl. 75; *Jahresb.* 1866, p. 284). The chlorhydrate acts very strongly on *ethyl iodide*, forming ethylsulphurous acid. With *ethylene bromide* it forms an acid having the composition $C^2H^4Br.SO^3H$ (Wroblevsky, *Zeitschr. f. Chem.* [2] v. 280). With *benzene* it forms sulphobenzene, together with phenyl-sulphurous acid and phenyl-sulphurous chloride (Knapp, *ibid.* 41):

$$SO^2.HO.Cl + C^6H^6 = \underset{\text{Phenyl-sulphurous acid.}}{C^6H^5.SO^2.OH} + HCl \text{ or } \underset{\text{Phenyl-sulphurous chloride.}}{C^6H^5.SO^2.Cl} + H^2O$$

$$SO^2.HO.Cl + 2C^6H^6 = \underset{\text{Sulphobenzene.}}{C^6H^5\text{—}SO^2\text{—}C^6H^5} + H^2O + HCl.$$

The corresponding compound *sulphuric chlorethylate*, $SO^2Cl(OC^2H^5)$, produced by direct combination of SO^3 and C^2H^5Cl, was discovered by R. Williamson in [illegible] (v. 576), and has lately been further examined by Purgold (*Compt. rend.* lxvii. 451; *Ann. Ch. Pharm.* cxlix. 124), who seems to be quite unacquainted with Williamson's experiments. It is a pungent, oily, strongly refracting liquid, having a sp. gr. of 1·3790 at 0°; 1·3556 at 27°; 1·3240 at 61°. Expansion-coefficient = 0·00[illegible] between 0° and 27°, and 0·007155 between 27° and 61°. Heated to 100° with water in a sealed tube, it yields sulphuric acid, hydrochloric acid, ethyl iodide, and a little ethyl chloride; with alcohol, a similar reaction, but the hydrochloric acid and the alcohol reproduce ethyl chloride. With a concentrated solution of sodium acetate it yields ethyl acetate, sodium sulphate, and free acetic acid:

$$SO^2ClOC^2H^5 + 2C^2H^3O(ONa) + H^2O = C^2H^3O(OC^2H^5) + SO^4Na^2 + HCl + C^2H^3O(OH).$$

When liquid ethyl chloride is agitated with sulphuric anhydride in a sealed tube, and the product is treated with water, an acid, $C^2H^3(OH)(OH)(SO^3)^2$, is formed, the potassium salt of which crystallises in beautiful white needles (Purgold).

Chlorosulphuric Anhydride or ***Pyrosulphuric Chloride.*** $S^2O^5Cl^2$.—This compound, which Rose obtained by the action of sulphuric anhydride on sulphur chloride, S^2Cl^2 (v. 571), is likewise produced, together with phosgene, by dissolving the anhydride in excess of carbon tetrachloride, and heating the solution in the water-bath:

$$2SO^3 + CCl^4 = S^2O^5Cl^2 + CCl^2O.$$

If the mixture of sulphuric anhydride and carbon tetrachloride be heated to 100° with *benzene*, and the product treated with water, it yields hydrochloric acid, sulphobenzide, phenylsulphurous acid, and benzoic acid (Schützenberger, *Zeitschr. f. Chem.* [2] v. 631).

Pyrosulphuric chloride is also formed, together with sulphuric chlorhydrate and carbon monoxide, by the action of sulphuric anhydride on chloroform. It boils at 144°–148°. The corresponding bromide is obtained in like manner with bromoform (Armstrong, *Zeitschr. f. Chem.* [2] vi. 247).

METALLIC SULPHATES. ***Aluminium Sulphate.***—On the preparation and testing of this salt for technical purposes, see Fleck (*J. pr. Chem.* xcix. 243; *Bull. Soc. Chim.* [2] viii. 39); Stein (*Zeitschr. anal. Chem.* v. 35); Giseke (*Dingl. pol. J.* clxxxiii. 43; *Bull. Soc. Chim.* [2] vii. 361; *Jahresb.* 1866, pp. 788, 856; 1867, p. 910).

Barium Sulphates.—The normal salt dissolves abundantly in hydrogen sulphate, H^2SO^4, at the boiling heat, especially when recently precipitated (100 pts. of the acid dissolve 11 to 12 pts. barium carbonate); the saturated solution does not deposit anything on cooling, but on evaporation yields the normal salt in crystalline granules. At 100°, normal barium sulphate dissolves still more easily in the strong acid, the solution becoming turbid at a higher temperature and depositing a white powder. On digesting the acid at a somewhat higher temperature with excess of the normal salt, *anhydrous acid barium sulphate*, $BaH^2(SO^4)^2$ or $BaSO^4.2H^2SO^4$, crystallises out in delicate shining prisms. When the solution of the normal salt in strong sulphuric acid is exposed to moist air, it deposits the *hydrated acid salt*, $BaH^2(SO^4)^2 + 2H^2O$, in slender soft asbestos-like needles (Schultz).

Bismuth Sulphates.—*Bismuth-ammonium Sulphate*, $Bi'''(NH^4)(SO^4)^2 + 4H^2O$, is prepared by adding a strong solution of acid ammonium sulphate to a solution of 109 pts. bismuth in 100 pts. nitric acid (3 mol. of the acid ammonium sulphate to 1 mol. bismuth nitrate), and separating the crystalline precipitate from the mother-liquor by pressure between filter-paper. It crystallises in six-sided tables, dissolves easily in hydrochloric and in nitric acid, less easily in strong sulphuric acid and in hot dilute acids. By prolonged digestion with cold acetic or dilute sulphuric acid it is resolved into acid ammonium sulphate and *bismuth-hydrogen sulphate* or *acid bismuth sulphate*, $Bi'''H(SO^4)^2 + H^2O$, which latter partly dissolves and separates from the solution on warming in microscopic needles, partly remains as an insoluble residue. Both this salt and the ammonium double salt are decomposed by prolonged boiling with water, leaving the monoacid salt $SO^3.Bi^2.O^4$, or *bismuth oxysulphate*,

$$\overset{\prime\prime\prime}{Bi^2}\left\{\begin{matrix}SO^4\\O^2\end{matrix}\right..$$

Bismuth-sodium sulphate, prepared like the ammonium salt, separates immediately as a crystalline precipitate made up of groups of microscopic needles. Its composition, neglecting a small and variable amount of water, is approximately represented by the formula $Bi^4Na^6(SO^4)^9$, and differs therefore both from that of the ammonium

salt, and from that of the potassium salt, $BiK^3(SO^4)^3$ (Lüddecke, *Ann. Ch. Pharm.*
277).

A *tetrammonio-cadmium sulphate*, $SO^4Cd.4NH^3$, is obtained by mixing cadmium
sulphate with a quantity of strong ammonia sufficient to redissolve the precipitate
irst produced, then adding a double volume of absolute alcohol containing ammonia,
and agitating. A thick liquid then separates, which, after being shaken with the
upernatant solution, solidifies in a few days to a crystalline powder. On separating
his powder from the liquid, redissolving it in strong aqueous ammonia, and covering
he solution with ammoniacal alcohol, the salt $SO^4Cd.4NH^3 + 5H^2O$ is deposited
n a few days in short hexagonal prisms with predominant perpendicular end-face,
ometimes also with a di-hexahedron of another order; cleavable parallel to the
erpendicular end-face. They give off ammonia, and crumble to a white powder on
xposure to the air, dissolve easily in ammonia and in hydrochloric acid, and are
ecomposed by water, with separation of a flocculent gelatinous precipitate, while
mmonium sulphate passes into solution (G. Müller, *Ann. Ch. Pharm.* cxlix. 70).

Calcium Sulphates.—Pulverised gypsum heated with water in sealed tubes to
40°–160° is converted into a coherent crystalline mass of the salt $2CaSO^4.H^2O$,
hich is not altered by prolonged heating, but is reconverted into gypsum in the cold.
the water be replaced by a saturated solution of sodium chloride (by enclosing
eces of rock-salt in the tube) the gypsum crystals are converted at 125°–130° into
milk-white porcelain-like mass, consisting of interlaced crystals of anhydrite, which
also reconverted into gypsum in the cold. At comparatively high temperatures,
erefore, solution of sodium chloride (and calcium chloride more slowly) withdraws
ater from gypsum, but at ordinary temperatures anhydrite takes water from a solu-
on of sodium chloride. Consequently gypsum dehydrated at 126° hardens in
ntact with solution of sodium chloride. This reaction may perhaps explain the
currence of masses of anhydrite in beds of rock-salt (Hoppe-Seyler, *Pogg. Ann.*
xvii. 161). When an aqueous solution of gypsum and magnesium bicarbonate is
aporated, the calcium sulphate, in consequence of the decomposition of the latter, is
ewise decomposed, forming calcium carbonate and magnesium sulphate. If, how-
er, the evaporation takes place at ordinary temperatures in an atmosphere containing
bonic acid, the calcium sulphate crystallises from such solutions without alteration.
is may account for the association of gypsum with dolomite (T. S. Hunt, *Bull. Soc.
im.* [2] viii. 181). From experiments with pure native gypsum, Church (*ibid.* ix.
3) finds that 1 pt. of $CaSO^4.2H^2O$ dissolves in 443 pts. water at 13·7°, in 447 pts.
14·2°, in 421 pts. at 20·2°, in 419 pts. at 21·2°, and at 18·7° in 445 pts. water
urated with carbonic acid.—Boiling concentrated sulphuric acid dissolves about ten
es its weight of normal calcium sulphate, and the solution when evaporated, first
lds granular anhydrous crystals of the normal salt, and afterwards solidifies to a
ss of flat silky prisms of the salt $CaH^6(SO^4)^4$ or $CaSO^4.3H^2SO^4$. This salt melts
little above 100° to a white pasty magma, probably with formation of the acid
described by Berzelius (Schultz, *Pogg. Ann.* cxxxiii. 137).

obalt Sulphate.—When a concentrated solution of this salt is gradually poured
ordinary sulphuric acid, a peach-blossom-coloured pulverulent precipitate soon
rates, having the composition $CoSO^4.4H^2O$ (Fröhde, *J. pr. Chem.* xcix. 63).

opper Sulphates.—On the solubility of normal cupric sulphate in water, see
on (*Jahresb.* 1866, p. 63); Gerlach (*ibid.* 129). On its efflorescence: Pape (*ibid.*
7, p. 2). On the refracting power of its solution: Fouqué (*ibid.* 97).
ormal cupric sulphate dissolves but sparingly in boiling concentrated sulphuric
, and crystallises out again on evaporation or on cooling, as anhydrous salt.
n a solution not saturated at the boiling heat, an acid salt appears to separate on
ng (Schultz).

asic Salts.—According to Reindel (*J. pr. Chem.* c. 1), the pale green basic salt
ipitated by the potash from excess of cupric sulphate at the boiling heat or at
50°, has the composition $7CuO.2SO^3 + 7H^2O$ or $2CuSO^4.5CuO + 7H^2O$.
same salt is formed when potassio-cupric sulphate is repeatedly washed with hot
r; also by digesting cupric oxide precipitated at the boiling heat with a solution
pric sulphate: the oxide prepared by igniting the nitrate remains unaltered when
treated. The blue-green precipitate is not attacked by boiling water or by boiling
ions of cupric sulphate; but it dissolves easily in acids and is converted by
h into the black hydrate $3CuO.H^2O$. It does not lose water at 100°, but is
rted at 150° into the pentahydrate $2CuSO^4.5CuO + 5H^2O$, and decomposes at
her temperature, leaving a residue from which boiling water extracts the normal

The blue-green precipitate thrown down from excess of cupric sulphate by
nia at the boiling heat has, according to Reindel, the composition $6CuO.2SO^3$
H^2O or $2(CuSO^4.2CuO).5H^2O$. It remains unaltered at 250°, but decomposes

at a higher temperature, like the preceding salt. Sodium carbonate under the same circumstances throws down a pale green sulphate consisting of $3CuO.SO^3 + 2H^2O$ or $CuSO^4.2CuO + 2H^2O$. This compound, which remains unaltered up to [illegible], appears to be likewise produced by prolonged boiling of zinc oxide with a solution of cupric sulphate. None of these basic salts give up the whole of their sulphuric acid even on prolonged ignition.

Indium Sulphate.—See INDIUM (p. 732).

Iron Sulphates.—On the specific gravity of solutions of ferrous sulphate, see Gerlach (*Jahresb.* 1866, p. 128). F. Muck (*J. pr. Chem.* xcix. 103; *Jahresb.* 1866, p. 241) has examined the alterations which take place in solutions of ferrous sulphate on exposure to the air. He finds that in the earlier stages of the oxidation the solution contains normal ferric sulphate, $Fe^2O^3.3SO^3$, and even free sulphuric acid, but ultimately the basic salt $Fe^2O^3.2SO^3$, distinguished by its deep brown-red colour. At the same time the deposit becomes progressively richer in acid, without, however, attaining the composition $2Fe^2O^3.3SO^3$, assigned to it by Wittstein (v. 595). The products of the oxidation vary with the continually changing composition of the solution, and cannot therefore be reduced to any simple expression. The basic ferric sulphates occurring as natural products are partly precipitates of this kind, partly dried-up mother-liquors.

Lead Sulphates.—According to Boussingault (*Compt. rend.* lxiv. 1159) normal lead sulphate is completely resolved at a white heat into PbO and SO^3. According to Rodwell (*Chem. News*, xv. 137), the same salt heated to redness in a current of dry ammonia gas is decomposed in the manner represented by the equation:

$$7PbSO^4 + 20NH^3 = 3PbS + 2Pb^2S + 22H^2O + 2(NH^4)^2SO^3 + 8N^2.$$

100 pts. of strong sulphuric acid dissolve about 6 pts. of normal lead sulphate, and a hot-saturated solution left to cool deposits the same salt in shining laminæ; but by slow evaporation in moist air a hydrated acid salt, $PbH^2(SO^4)^2 + H^2O$, is obtained (Schultz).

Lithium Sulphates.—On the crystalline forms of normal lithium sulphate, lithio-potassic and lithio-sodic sulphate, see LITHIUM (p. 792). *Acid lithium sulphate*, $LiHSO^4$, crystallises in prisms from a solution of the normal salt in sulphuric acid of sp. gr. 1·6 to 1·7 (from more dilute acid, the normal salt separates again). The acid salt melts at 160° (Schultz).

Magnesium Sulphates.—The extraction of the normal salt from the mother-liquors of the salt-gardens at Camargue is described by Balard (*Bull. Soc. d'Encouragement*, 1865, xii.; *J. Pharm.* [4] iii. 179; *Jahresb.* 1866, p. 847). On the preparation of this salt, see also Mirus (*N. Jahrb. Pharm.* xxvii. 92) and Swindells (*Chem. News*, xv. 178). It dissolves but slightly in boiling hydrogen sulphate, H^2SO^4 (2 pts. in 100 pts. of the acid), more abundantly in acid of sp. gr. 1·7, and this solution when cooled or further evaporated at the boiling heat, deposits the acid salt, $MgH^2(SO^4)^2$ or $MgSO^4.H^2SO^4$, in prisms differing by their infusibility from the following salt. The *triacid salt*, $MgH^6(SO^4)^4$ or $MgSO^4.3H^2SO^4$, crystallises on cooling from a solution of the normal salt in boiling hydrogen sulphate, in small shining tables which partly melt and decompose when heated (Schultz).

Manganous Sulphates.—The normal salt dissolves in about 20 pts. of boiling hydrogen sulphate, and the solution on beginning to cool deposits the *acid salt*, $MnH^2(SO^4)^2$, in asbestiform prisms, which do not melt when heated; they are generally, however, mixed with the hexhydromanganous salt, $MnH^6(SO^4)^4$, which separates from the same solution below 100° in small crystalline laminæ melting with decomposition when heated. Sulphuric acid of sp. gr. 1·6 dissolves the normal salt more readily when heated, and the solution on cooling deposits the hydrated acid salt, $MnH^2(SO^4)^2 + H^2O$, in nacreous laminæ.

Potassium Sulphates.—On the solubility of the normal salt, see *Jahresb.* 1866, pp. 59, 67. The *trihydropotassic* or *hyperacid salt*, $KH^3(SO^4)^2$ or $KHSO^4.H^2SO^4$, is formed by fusing the normal salt with less than 3 mol. hydrogen sulphate: the mixture solidifies after a while to a crystalline cake, consisting for the most part of this hyperacid salt. It is obtained in isolated crystals when the solution of the normal salt in less than 5 mol. hydrogen sulphate is made to crystallise by introducing into it a granule of the solidified mass. It crystallises in long shining prisms melting at about 95°. It does not solidify from fusion even when cooled to a low temperature, but it solidifies, with considerable rise of temperature, when brought in contact with a crystal of the solid hyperacid salt, but not by contact with a crystal of the normal or acid salt (Schultz).

Silver Sulphates.—The *acid salt*, or *hydro-argentic sulphate*, $AgHSO^4$, crystallises in faintly yellowish prisms from a solution of the normal salt in less than three parts of hydrogen sulphate. A solution of the normal salt in 8 or 10 pts. acid of sp. gr. 1·6 to 1·7 yields *trihydro-argentic sulphate*, $AgH^3(SO^4)^2 + H^2O$, in prisms. Larger crystals of this salt are obtained by dissolving the normal salt in 6 to 10 pts. hydrogen sulphate, and leaving the solution to become diluted by exposure to moist air. The salt begins to melt at 100°, becomes perfectly fluid at 150°, and solidifies on cooling to a broadly laminar crystalline mass, gradually changing into small, flat, shining prisms. A warm solution of the normal salt in only 4 to 6 pts. of acid of sp. gr. 1·75 deposits on cooling the *hexhydro-tetrargentic salt*, $Ag^4H^6(SO^4)^5 + 2H^2O$, in nacreous laminæ. Other silver sulphates appear also to separate from variously concentrated solutions in sulphuric acid, but their preparation does not always succeed. The *normal salt*, Ag^2SO^4, likewise crystallises in yellowish rhombic octohedrons from a cooled solution in somewhat diluted sulphuric acid, or in the more concentrated acid when the liquid is left to absorb water gradually from the air (Schultz).

Trihydro-sodic Sulphate, $NaH^3(SO^4)^2$, crystallises on cooling from a hot-prepared solution of the normal sodium salt in less than 7 pts. of hydrogen sulphate; it resembles the corresponding potassium salt, and melts at about 100°.

Strontium Sulphates.—According to Boussingault (*Jahresb.* 1867, p. 161) the ormal salt is decomposed at a full white heat into SrO and SO^3. According to Darmtädt (*ibid.* 152) it is partially decomposed at lower temperatures. An earthy mineral ontaining 86 p. c. of this salt (together with lime, magnesia, clay, &c.) occurs in Upper Silesia, where it is used as a manure, like gypsum (Lunge, *Chem. News*, xv. 18). The *anhydrous acid salt* and the *hydrated acid salt*, $SrH^2(SO^4)^2 + H^2O$, are repared like the corresponding barium salts (Schultz).

Thallium Sulphates.—The *normal thallious salt*, Tl^2SO^4, may be fused without lteration in a covered crucible at the volatilising temperature of common salt; heated n an open vessel, or by the blowpipe-flame, it is decomposed, with evolution of sulhurous oxide and formation of thallic oxide, Tl^2O^3. Ignited in a current of hydrogen, melts, blackens, gives off sulphur, and finally leaves a mixture of metallic thallium, allium sulphide, and thallious sulphate. An *acid salt* is precipitated by water from solution of thallium in strong sulphuric acid, as an amorphous powder, the aqueous lution of which first yields crystals of the normal salt, and afterwards thick short isms of the acid salt (Carstanjen, *Jahresb.* 1867, p. 279).

Titanium Sulphates.—See TITANIUM.

Zinc Sulphates.—According to Reindel (*Zeitschr. f. Chem.* [2] v. 508) the prepitate formed by boiling zinc sulphate with ammonia has, when washed with water d dried over oil of vitriol, the composition $8ZnO.16H^2O.SO^3$; at 110°, $nO.7H^2O.SO^3$; at 200°, $8ZnO.6H^2O.SO^3$; at 250°, $8ZnO.H^2O.SO^3$. This last t yielded to cold water considerable quantities of the normal sulphate, $ZnO.SO^3$. does not appear, however, to be a mixture of normal sulphate and zinc hydrate; even after washing for six weeks with hot water it did not yield a residue free m sulphuric acid. The basic salt remaining after this treatment had when dried 100° the composition $9ZnO.12H^2O.SO^3$.

An ammoniacal zinc sulphate, $SO^4Zn.4NH^3 + 2H^2O$, prepared like the corrending cadmium salt (p. 1071), separates as a syrup which gradually changes to a stalline powder. At a winter temperature the solution yields crystals of another drate, $SO^4Zn.4NH^3 + 4H^2O$, which effloresce in the cold to a white powder, with tinual evolution of ammonia, and deliquesce on the slightest rise of temperature Müller, *Zeitschr. f. Chem.* [2] v. 250; vi. 96).

. **Thiosulphuric Acid.** $H^2S^2O^3 = \left.\begin{matrix}HS\\HO\end{matrix}\right\}SO^2$.—This is the acid commonly called osulphurous acid, produced by sulphuration of sulphurous acid, just as sulphuric is formed by oxidation of the latter. By some chemists, however, as already ed (v. 630), it has been represented by the simpler formula H^2SO^2, and regarded monobasic acid analogous to formic acid, H^2CO^2, this view being based partly on upposed formation by the reducing action of zinc, sodium, and other metals on hurous acid, partly on a statement of Rose that all hyposulphites contain water, h appears to be essential to their constitution, since it cannot be driven off without or decomposition; and, such being the case, the ordinary formula of a hypohite admits of being halved: *e.g.* $Na^2S^2O^3.H^2O = Na^2H^2SO^4 = 2NaHSO^2$. , however, showed in 1864 that the lead salt of this acid contains no water of allisation, and when dried at 100° has the composition PbS^2O^3; moreover that sium, sodium, and barium salts give off their water at about 215°, and decomwith separation of sulphur between 220° and 225°. These experiments of Pape potash (Wagner, *Chem. Centr.* 1861, p. 47). By fusion with potash it is converted into oxyquinone, $C^6H^4O^3$ (Malin, p. 893).

According to Löwe (*J. pr. Chem.* cvii. 296; *Zeitschr. f. Chem.* [2] vi. 128), the formula of rufigallic acid is $C^{14}H^8O^8$, and its formation from gallic acid is attended with the formation of a product of oxidation, the oxygen being supplied at the expense of the sulphuric acid: other dehydrating agents, zinc chloride for example, do not convert gallic into rufigallic acid. By strong potash solution, and especially by alcoholic potash, it is converted into a blue-black salt.

RUTIN. According to Spiess a. Sostmann (*Jahresb.* 1865, p. 587), this substance, $C^{25}H^{32}O^{17}$ (or $C^{25}H^{28}O^{15}$ $2H^2O$), is easily obtained from commercial Chinese yellow berries in grains (the undeveloped flower-buds of *Sophora japonica*, known as Waïfa), whereas Chinese yellow berries in pods (the fruit of *Gardenia radicans* and *G. florida*) contain, not rutin, but mannite.

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SACCHARIC ETHER. Crystallised ethyl saccharate gently heated with 4 mol. acetyl chloride, is converted into a crystalline compound, $C^{10}H^{10}O^8$, mixed with an oil insoluble in water. The crystalline body is perhaps formed in the manner shown by the equation:

$$\underset{\text{Saccharic acid.}}{C^6H^{10}O^8} + \underset{\text{Acetyl chloride.}}{4C^2H^3OCl} = \underset{\text{Crystalline compound.}}{C^{10}H^{10}O^8} + \underset{\text{Acetic acid.}}{2C^2H^4O^2} + 4HCl.$$

When the crystalline compound of ethyl saccharate and calcium chloride is heated to 100° with somewhat more than an equal weight of acetyl chloride, a gummy mass is formed which gives up to anhydrous ether an oil easily soluble in water and alcohol, and solidifying for the most part in the crystalline form over sulphuric acid. The crystals consist of *ethylic tetracetyl-saccharate*, $C^6H^4(C^2H^3O)^4O^8.(C^2H^5)^2$. This ether crystallises from alcohol in monoclinic prisms, melting at 61°, insoluble in water, soluble in alcohol and ether, and resinised by alcoholic potash (Baltzer, *Bull. Soc. Chim.* [2] x. 263).

SAFFRON (B. Weiss, *J. pr. Chem.* ci. 65).—When dried saffron, after exhaustion with ether, which removes a small quantity of a yellowish oil, is digested with water, gum, vegetable mucilage, inorganic salts, and sugar are dissolved, together with the unaltered colouring matter of the saffron; from this solution, the gum, mucilage, and inorganic salts may be precipitated by absolute alcohol; and the filtrate mixed with ether deposits the colouring matter mixed with small quantities of sugar and salts. This colouring matter, polychroïte, $C^{48}H^{60}O^{18}$ (?), forms an orange-yellow precipitate which dries up over sulphuric acid to a friable, ruby-coloured, deliquescent mass. It is inodorous, has a faint, sweetish taste, dissolves easily in water and in dilute alcohol, but is nearly insoluble in absolute alcohol. The aqueous solution is turned brown by hydrogen sulphide, and is decolorised by nitrous acid or chlorine. By dilute acids it is resolved into a red secondary colouring matter (crocin), sugar, and an aromatic oil having the characteristic odour of saffron. On heating its aqueous solution with dilute sulphuric acid (not in excess) in a retort through which a stream of hydrogen is passed, crocin separates as a red powder, while the oil distils over.

Crocin has the composition $C^{16}H^{18}O^6$; an orange-yellow lead salt precipitated from its alcoholic solution by lead acetate contains $(C^{16}H^{17}O^6)^2Pb$; a red substance very much like crocin, left undissolved by ether in the preparation of polychroïte, consists of $2C^{16}H^{18}O^6.3H^2O$. Crocin dissolves very sparingly in water, easily in alcohol and in dilute alkalis. From the alcoholic solution it is precipitated by ether, from solution in alkalis by acids, in purple-red flocks. Heated with strong potash-ley, it decomposes, with evolution of pungent vapours. With strong sulphuric acid it acquires a deep blue colour, gradually changing to violet and brown; nitric acid colours it green, changing to yellow-brown. Crocin suspended in water dissolves in nitric acid to a colourless liquid, without formation of oxalic acid; it is decolorised by chlorine; not affected by sulphurous acid.

rhombic crystals are formed, a further quantity of which is obtained on adding ammonia to the mother-liquor. They are nearly insoluble in cold water, and are decomposed by hot water, with evolution of ammonia and separation of brown flocks and a specular deposit on the glass; the cooled filtrate mixed with ammonia again yields blue crystals. These crystals have the composition $N^4H^{12}Na^4Cu^2S^8O^{12}$. Heated with potash-ley they yield a precipitate consisting of a cuproso-cupric hydrate, consisting when air-dried of $Cu^3O^2.2H^2O$, and after drying in a vacuum of $Cu^3O^2.H^2O$:

$$\underset{\text{Blue salt}}{N^4H^{12}Na^4Cu^2S^8O^{12}} + 4KHO = \underset{\substack{\text{Sodio-potassic}\\\text{thiosulphate}}}{4NaKS^2O^3} + 4NH^3 + Cu^2H^4O^4$$

(Siewert, *Bull. Soc. Chim.* [2] vii. 242; *Jahresb.* 1866, p. 256). Compare v. 633.

Sodio-platinous Thiosulphate, $Na^6Pt''(S^2O^3)^4 + 10H^2O$, is obtained by adding pulverised crystals of ammonium platinosochloride to a concentrated solution of sodium thiosulphate, mixing the yellow liquid with twice or three times its volume of absolute alcohol, separating the heavy oily layer, which gradually solidifies to a crystalline mass, from the colourless liquid, dissolving it in a small quantity of water, and reprecipitating with alcohol, taking care to leave a portion of the salt in solution. By a third precipitation from the aqueous solution, and washing with absolute alcohol, the salt is obtained nearly pure. After drying over oil of vitriol, it forms a compact, yellow, partly brownish mass, which does not exhibit distinct crystals under the microscope. It dissolves easily in water. The solution is not altered by caustic potash or soda even at the boiling heat, slowly by hydrochloric acid in the cold, quickly when heated, with evolution of sulphurous oxide and precipitation of platinum sulphide. Hydrogen sulphide does not precipitate the platinum, either from the neutral or from the cold acidulated solution. The same double salt appears to be formed by dissolving ammonium platinochloride in sodium thiosulphate, but it cannot be isolated in this manner on account of the great instability of the resulting solution (Schottländer, *Ann. Ch. Pharm.* cxl. 200). Its composition affords further and decisive confirmation of the bibasic character of thiosulphuric acid.

5. **Seleniosulphuric Acid.** $H^2SeSO^3 = \left.\begin{matrix}HSe\\HO\end{matrix}\right\}SO^2$. *Seleniohyposulphurous Acid. Seleniodithionous Acid.*—This acid, formed by addition of selenium to sulphurous acid, was first obtained as a potassium salt by Cloez (*Bull. Soc. Chim.* Dec. 13, 1861), and further examined by Rathke (*J. pr. Chem.* xcv. i.; *Jahresb.* 1865, p. 144). When elenium is digested with a solution of neutral potassium sulphite, and the easily lecomposible liquid, after being filtered from the selenium which separates on cooling nd dilution with water, is left to evaporate at ordinary temperatures, there crystallises out, first a sparingly soluble seleniferous salt in small shining prisms, afterwards much more soluble salt, which is the chief product of the reaction, while the excess of ulphite remains in the mother-liquor.

The more soluble seleniferous salt is potassium seleniosulphate, K^2SeSO^3. It is likeise formed, together with thiosulphate, when a solution of potassium selenide is mixed ith sulphurous acid. It crystallises readily, even from small quantities of solution, large very thin six-sided tables belonging to the rhombic system, which deliquesce moist air, and effloresce with partial loss of water over oil of vitriol. When heated ey turn brown and yield a polysulphide of potassium. Water separates selenium om them, and the filtered solution yields by evaporation crystals which again react the same way with water, so that by repeated crystallisation the whole of the seleniolphate may be decomposed; the liquid then contains seleniotrithionate. *Acids*, even lphurous acid, throw down the whole of the selenium from the aqueous solution; *rium chloride* and *baryta-water* precipitate barium sulphite and selenium; *calcium* d *manganese salts* give rise to a similar decomposition. With *ammoniacal silver ution* the seleniosulphate forms a precipitate of silver selenide together with potasm sulphate:

$$K^2SeSO^3 + Ag^2O = Ag^2Se + K^2SO^4.$$

eutral silver solution decomposes part of the acid at the same time into selenium sulphurous acid. *Mercuric cyanide* at the boiling heat forms mercuric selenide potassium sulphate; neutral *cadmium solutions* throw down white sparingly ble cadmium seleniosulphate, which is resolved by heat into cadmium selenide and huric acid. By digestion with recently precipitated *silver sulphide*, the seleniohate is easily and completely resolved into silver selenide and potassium thiosulphate. *ne* throws down selenium, which is oxidised by the excess of iodine. *Ferric chloride* ws down selenium, together with a brown precipitate containing iron.

The sulphites of sodium, ammonium, and magnesium react with selenium in the same manner as the potassium salt, the magnesium salt however very slowly. The seleniosulphates of sodium and ammonium are very unstable (Rathke).

6. **Dithionic Acid.** $H^2S^2O^6$.—According to Otto (*Ann. Ch. Pharm.* cxlvii. 187) this acid is reduced by nascent hydrogen (either by prolonged contact of the solution of its barium salt with sodium-amalgam, or by the action of zinc and hydrochloric acid) to sulphurous acid, even when the mixture is cooled to 0°. On the crystalline form of *lithium dithionate*, see LITHIUM SALTS (p. 792).

7. **Trithionic Acid.** $H^2S^3O^6$ (v. 639).—According to Saintpierre (*Bull. Soc. Chim.* [2] v. 245) the formation of this acid by Langlois' method (digesting acid potassium sulphite with sulphur) depends, not on the action of the free sulphur and of the oxygen of the air, but upon the resolution of the sulphurous acid into sulphur, sulphuric acid, and trithionic acid:

$$10KHSO^3 = 5K^2SO^4 + H^2S^3O^6 + S^2 + 4H^2O.$$

A dilute solution of acid potassium sulphite enclosed in a sealed tube and first heated in the water-bath, then left to itself for four years, was found to have deposited sulphur and to contain sulphuric and trithionic acids, but no sulphurous acid or any other oxygen-acid of sulphur. Langlois, on the other hand, without questioning the results obtained by Saintpierre with dilute solutions, calls attention to the fact that in his own mode of preparation, which supposes the use of a saturated solution of potassium sulphite containing crystals in excess, the sulphur certainly takes part in the reaction, inasmuch as the liquid soon acquires a yellowish colour, which it does not lose till the acid sulphite is wholly converted into trithionate; sulphuric acid is not formed in any considerable quantity. Langlois regards it as most probable that the sulphur first converts the sulphite into thiosulphate, and that this salt is then converted into trithionate, according to the equation:

$$2K^2S^2O^3 + 3SO^2 = 2K^2S^3O^6 + S.$$

Seleniotrithionic Acid. $H^2S^2SeO^6$ (Rathke, *J. pr. Chem.* xcv. 1; *Jahresb.* 1865, p. 146).—The potassium salt of this acid is the less soluble of the two salts, formed, as already mentioned (p. 1075), by digesting selenium with neutral potassium sulphite. It is obtained in greatest quantity, but contaminated with 6 to 11 p. c. potassium sulphate, when the solution contains a certain quantity of acid potassium sulphite. It is also formed (like the trithionate) by digesting selenium with a solution of acid potassium sulphite at 50° to 60°, but only in small quantity, as it is easily decomposed by heat into selenium, sulphurous acid, and neutral potassium sulphite. It is moreover produced by evaporating a solution of seleniosulphate and acid sulphite of potassium (the thiosulphate formed at the same time may give rise to trithionate), and even crystallises in small quantity from neutral or alkaline solutions of selenium in sulphites, inasmuch as a certain quantity of acid sulphite is produced by the action of atmospheric carbonic acid. On the other hand, it is not formed by the action of free sulphurous acid on potassium seleniosulphate, or of selenious acid on the thiosulphate (in the latter case selenium and sulphur are separated, and potassium trithionate is formed on evaporation). The seleniotrithionate is obtained in greatest purity by mixing a solution of the thiosulphate containing excess of neutral sulphite with a concentrated solution of selenious acid. The liquid then becomes warm, and immediately yields a precipitate consisting of slender needles, which increases on cooling, and may be freed by washing with cold water from all but traces of foreign salts.

The seleniotrithionate obtained by the first process forms very thin prisms having a vitreous lustre and permanent in the air. It is anhydrous, forms a clear solution in water, but decomposes in solution in course of time, partly into potassium dithionate and free selenium (which explains the mode of formation of the dithionate mentioned in vol. v. p. 637), partly into selenium, potassium sulphate, and free sulphurous acid, the latter mode of decomposition taking place chiefly when heat is applied, or on evaporation in a vacuum over oil of vitriol. *Acids* do not precipitate the solution in the cold; but at the boiling heat they precipitate selenium and eliminate sulphurous acid. The pure seleniotrithionate does not yield a precipitate with *sulphurous acid* or *barium chloride*, whereby it is distinguished from the seleniosulphate. Heated with *ammoniacal silver solution* it is decomposed in the manner shown by the equation:

$$K^2S^2SeO^6 + Ag^2O = Ag^2Se + K^2SO^4 + SO^2.$$

With *mercuric cyanide* under similar circumstances it yields mercuric selenide (Rathke).

SULPHUR SALTS. The following double sulphides have been obtained by fusing 1 pt. of a heavy metal with 6 pts. of potassium or sodium carbonate, and 6 pts. of sulphur, and lixiviating the fused mass with water (R. Schneider, *Pogg. Ann.* cxxxvi. 460; cxxxviii. 299, 604; *Zeitschr. f. Chem.* [2] v. 629; vi. 270).

Potassium-bismuth Sulphide, $K^2Bi^2S^4 = K^2S.Bi^2S^3$, crystallises in light steel-grey shining needles; the *sodium salt*, of similar composition, is obtained as a steel-grey mass made up of small crystals.

Potassio-cuproso-cupric Sulphide, $K^2Cu^6S^6 = K^2S.3(Cu^2)''S.2CuS$, forms shining steel-blue laminæ, which, when heated in a stream of hydrogen, give off one-sixth of their sulphur, the cupric sulphide being reduced to cuprous sulphide. *Sodio-cuproso-cupric Sulphide*, $Na^2Cu^3S^3 = Na^2S.(Cu^2)''SCuS$, forms grey-blue needles, quickly decomposed by moist air, reacting with hydrogen like the potassium salt.

Potassium-iron Sulphide, $K^2Fe^2S^4$, forms purple-brown, flexible, shining needles, permanent in the air at ordinary temperatures, bearing a red heat in a close vessel without alteration, but oxidising to ferric oxide and potassium sulphate when heated in contact with the air. Dilute acids decompose it, with evolution of hydrogen sulphide and separation of sulphur. By ignition in hydrogen it is reduced to $K^2Fe^2S^3$ or $K^2S.2FeS$, which dissolves in hydrochloric acid without separation of sulphur. *Sodium-iron Sulphide* is a dark copper-coloured compound which when dried over sulphuric acid has the composition $Na^2Fe^2S^4 + 4H^2O$. On suspending it (or the potassium salt) in water and adding solution of silver nitrate, a precipitate of silver-iron sulphide, Ag^4FeS^4, is formed, and ferrous nitrate passes into the solution, together with sodium-nitrate. Hence Schneider concludes that the two atoms of iron in the sodium (or potassium) salt have different equivalent values, and that the reaction just mentioned takes place as represented by the equation:

$$Na^2Fe''Fe^{iv}S^4 + 4AgNO^3 = Ag^4Fe^{iv}S^4 + Fe''(NO^3)^2 + 2NaNO^3.$$

The silver salt, $Ag^4Fe^{iv}S^4$, is black and crystalline, is attacked only by concentrated hydrochloric acid, and when ignited yields a sublimate of sulphur and a residue consisting of ferrous sulphide and metallic silver.

Potassio-ferroso-cuproso-cupric Sulphide, $K^2Fe''(Cu^2)''Cu''S^4$, obtained by fusing 10·25 to 10·5 pts. copper with 3 pts. iron, 72 pts. potassium carbonate, and 72 pts. sulphur, and lixiviating, forms blue and red crystalline lamellæ, which give off ¼ of their sulphur when ignited in hydrogen. A corresponding sodium salt is obtained in like manner.

Potassio-platinoso-sulphoplatinate, $K^2Pt^3Pt^{iv}S^6$, is obtained by fusing 1 to 2 pts. platinum-sponge with 6 pts. potassium carbonate and 6 pts. sulphur, and lixiviating, in large reddish crystals, having a sp. gr. of 6·44 (at 15°); permanent in the air at ordinary temperatures; decomposed by gaseous hydrogen chloride, with evolution of hydrogen sulphide; dissolved by aqueous hydrochloric acid, with formation of potassium chloride and without evolution of hydrogen sulphide, evidently producing the compound $H^2\overset{''}{Pt}{}^3Pt^{iv}S^6$. The hydrogen is however quickly expelled, and an atom of sulphur unites ith a portion of the platinous sulphide, forming the compound $PtS.PtS^2$. This compound retains water till heated to 120°; it is steel-grey, crystalline, and has a sp. gr. f 5·52. Potassio-platinoso-sulphoplatinate heated in a stream of hydrogen gives off of its sulphur, leaving a mixture of $K^2S.PtS$ with metallic platinum. *Sodio-platioso-sulphoplatinate*, $Na^2\overset{''}{Pt}{}^3Pt^{iv}S^6$, is exactly analogous to the potassium salt.

Potassio-platinous Sulphostannate, $K^2\overset{''}{Pt}{}^3Sn^{iv}S^6$, is obtained, by fusing 2 pts. platinum ith 1 pt. stannic sulphide, 3 pts. potassium carbonate, and 3 pts. sulphur, and lixiviting with water, as a cochineal-red crystalline powder appearing under the microscope s a mass of six-sided tables. It gives off ⅔ of its sulphur when heated in a stream of ydrogen, and when treated with dilute hydrochloric or acetic acid gives up all its otassium, and is converted into $H^2\overset{''}{Pt}{}^3Sn^{iv}S^6$. This latter compound oxidises in the r, the hydrogen going off as water, and the compound $\overset{''}{Pt}{}^3Pt^{iv}Sn^{iv}S^6$ being left.

Sodio-platinous sulphostannate is obtained by fusing 1 pt. platinum and ½ pt. stannic lphide with 3 pts. potassium carbonate, ⅙ pt. sodium carbonate, and 3 pts. sulphur. y fusing 1 pt. platinum with 6 pts. sodium carbonate and 6 pts. sulphur, a mass aversed by red crystals is obtained, which cannot be washed with water containing r without decomposing the crystals; these crystals consist of $Na^4\overset{''}{Pt}{}^3Sn^{iv}S^6$. When bjected to prolonged washing with water, they leave a black-brown residue of platinic lphide, PtS^2. When washed with de-aërated water and treated with silver nitrate they yield a grey mass consisting of *argento-platinous sulphostannate*, $Ag^4\overset{ii}{Pt}{}^2Sn^{iv}S^6$, which is permanent in the air, is not decomposed by hydrochloric acid, but easily by nitric or nitromuriatic acid. The red sodium salt treated with thallious sulphate yields *thallio-platinous sulphostannate*, $Tl^4\overset{ii}{Pt}{}^2Sn^{iv}S^6$. The sodium may also be replaced by various bivalent metals, as iron, manganese, cadmium, copper, lead, and mercury.

SYENITE. For analyses of this rock from various localities, see *Jahresb.* 1867, pp. 1020, 1028.

SYRINGA. Analyses of the ash of the leaves and flowers of the lilac (*Syringa vulgaris*) have been published by Wittstein (*Vierteljahrsschr. pr. Pharm.* xvi. 81): A. Leaves of the white-flowered variety: amount of ash after drying at 110° = 4·359 p. c.;—B. Leaves of the violet-flowered variety: ash at 110° = 4·922 p. c.;—C. White flowers (without calyx): ash at 110° = 5·76 p. c.;—D. Violet flowers (without calyx): ash at 110° = 4·286 p. c.:

	A	B	C	D
NaCl . .	3·100	0·543	3·247	0·108
KCl . .	—	—	—	1·564
K^2O . .	25·048	23·347	37·109	39·020
Na^2O . .	12·381	12·500	3·963	—
CaO . .	16·344	14·755	6·511	6·688
MgO . .	7·601	6·255	4·372	5·648
Al^2O^3 . .	0·195	0·188	0·135	0·240
Fe^2O^3 . .	0·360	2·039	0·446	0·424
MnO . .	—	0·481	—	0·119
SO^3 . .	0·613	2·719	3·648	3·281
P^2O^5 . .	10·233	25·352	18·591	27·355
SiO^2 . .	2·865	6·100	3·093	3·848
CO^2 . .	21·050	5·310	18·567	11·428
	99·790	99·589	99·682	99·723

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TABERGITE. This mineral, from Taberg in Wermeland, Sweden, has been analysed by C. W. Fuchs (*Jahrb. Min.* 1867, p. 822), who finds it to contain:

SiO^2	Al^2O^3	FeO	MnO	MgO	CaO	K	Na	H^2O	F	
32·95	13·08	13·72	0·07	26·83	0·95	0·33	1·25	11·34	0·97	= 101·49

leading to the formula $3[7(2MgO.SiO^2) + 2(Al^2O^3.SiO^2) + 10H^2O] + 2(K;Na)F$. The mineral, which is intermediate between chlorite and magnesia mica, is broadly laminar, perfectly cleavable, with nacreous to fatty lustre on the cleavage-faces. Predominant colour bluish-green, with silver-white to blackish spots. Hardness 2 to 2·5. Sp. gr. 2·813. Streak greenish-white.

TALTALITE. The mineral from Atacama so called by Domeyko (v. 657) is according to Ulex (*J. pr. Chem.* xcvi. 37) a mixture of atacamite, malachite, red hæmatite, and limestone, traversed by crystals of turmalin, or according to Pisani (*Sill. Am. J.* [2] xliii. 37) a mixture of turmalin and cupric oxide.

TAENITE. Laminar nickel-iron containing 13·2 p. c. nickel, occurring in meteorites (G. Rose, *Jahresb.* 1865, p. 945).

TANTALATES. On the classification and analysis of natural tantalates, see Blomstrand (*Jahresb.* 1865, p. 895; 1866, p. 944).

TANTALUM. Ta = 182.—The specific gravity of pure tantalic oxide or anhydride, Ta^2O^5, precipitated from tantalic chloride by ammoniacal water, and gently ignited, has been found by Deville a. Troost (*Compt. rend.* lxiv. 294) to be 7·35.

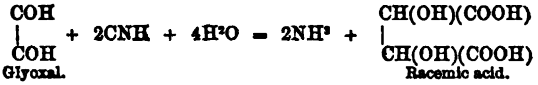
The same chemists have redetermined the vapour-density of tantalic chloride, $TaCl^5$, and found it to be 12·8 at 360°, 13·0 at 440; calc. = 12·5. The pure chloride is pale yellow and crystallisable, melts at 211·3°, and boils at 241·6° under a pressure of 753 mm. Its vapour passed over ignited tantalic oxide does not form an oxychloride.

An alloy of tantalum and aluminium, $TaAl^3$, is obtained by fusing potassiotantalic fluoride with aluminium-foil in a crucible lined with charcoal, and treating the resulting regulus with hydrochloric acid to dissolve the excess of aluminium. The alloy then remains as a crystalline powder, having a sp. gr. of 7·02. It is but slightly attacked by strong boiling hydrochloric acid, not at all by nitric, nitromuriatic, or dilute sulphuric acid; but it is dissolved by hydrofluoric acid at ordinary temperatures, by strong sulphuric acid at the boiling heat, and by fused acid potassium sulphate (Marignac, *Bull. Soc. Chim.* [2] ix. 465).

Respecting Hermann's criticisms on Marignac's views of the constitution of the tantalum compounds, see *J. pr. Chem.* c. 385; *Bull. Soc. Chim.* [2] viii. 171;—for Marignac's reply: *J. pr. Chem.* ci. 459; *Zeitschr. f. Chem.* [2] iv. 91; *Jahresb.* 1867, p. 209.

TARCONINE. A product of the decomposition of narcotine tri-iodide (p. 865).

TARTARIC ACIDS. Paratartaric or racemic acid (or inactive tartaric acid) is formed by boiling glyoxal with dilute hydrocyanic acid and a small quantity of hydrochloric acid in a retort with upright condenser, adding hydrochloric acid from time to time. The liquid neutralised with milk of lime yields a calcium salt consisting essentially of calcium racemate (or inactive tartrate). The acid separated from it exhibits all the characters of ordinary racemic acid, but it is doubtful whether it is resolvable into dextro- and lævo-tartaric acid. The mode of formation may be represented by the equation:



$$\begin{array}{c}COH\\ |\\ COH\end{array} + 2CNH + 4H^2O = 2NH^3 + \begin{array}{c}CH(OH)(COOH)\\ |\\ CH(OH)(COOH)\end{array}$$

Glyoxal. Racemic acid.

This mode of formation establishes the constitutional formula of the acids of the artaric acid group. The acid obtained as above is quite distinct from Schöyen's lycotartaric acid (p. 650) (Strecker, *Zeitschr. f. Chem.* [2] iv. 216). Paratartaric cid is also formed, together with dibromosuccinic acid, by the action of bromine and ater on phenaconic acid (Carius, p. 905). The paratartaric acid thus obtained agrees ith natural racemic acid in crystalline form and in the form and composition of its alcium salt (v. 37).

When tartaric acid is subjected to *dry distillation*, an oily distillate of pyrotartaric id is obtained between 170° and 210°, mixed with needles of pyrotritartaric acid, $^7H^8O^3$:

$$3C^4H^6O^6 = C^7H^8O^3 + 5CO^2 + 5H^2O$$

Vislicenus a. Stadnicki, p. 981).

Tartaric acid subjected to *electrolysis* yields at the positive pole carbon dioxide and onoxide, together with oxygen; the solution contains acetic acid. A solution of 68 s. neutral potassium tartrate in 32 pts. water yields chiefly carbon dioxide, with all quantities of carbon monoxide and oxygen, and deposits acid tartrate. A solun containing 4 mol. neutral potassium hydrate yields the same gases, together with race of ethane, and potassium acetate is formed in the liquid (Bourgoin, *Ann. Ch. ys.* [4] xiv. 157; *Jahresb.* 1867, p. 385).

Tartaric acid is decomposed by heating with *water* to 180° in a sealed tube, the st product formed being probably pyrotartaric acid, but it undergoes further alteraon (Morkownikoff a. Purgold, *Zeitschr. f. Chem.* [2] iii. 264).

When tartaric acid is heated with *hydrochloric acid* in sealed tubes, decomposition gins at 125°, and at 180° the tartaric acid is completely resolved into carbon dioxide, bon monoxide, pyrotartaric acid, and a carbonaceous residue. Paratartaric acid ilarly treated also yields pyrotartaric acid, the decomposition beginning at 130° and ng completed at 160° (Geuther a. Riemann, *Zeitschr. f. Chem.* [2] v. 318).

When tartaric acid mixed with a solution of *leuteocobaltic chloride* (1 pt. of the salt 5 pts. water) is boiled with potash or soda, the yellow solution becomes first green, n bluish-violet. This reaction may serve for the detection of tartaric acid in presence of some of the more ordinarily occurring organic acids. Malic, formic, benzoic, succinic, citric, acetic, and oxalic acids treated in like manner yield a precipitate of cobaltous hydrate, the acid being simply transferred to the potash. To apply this reaction, the tartaric acid, and any oxalic acid that may be present, are precipitated by calcium chloride and ammonia, the washed precipitate is boiled with a strong solution of sodium carbonate, and the filtrate, freed from carbonic acid by means of hydrochloric acid, is mixed with caustic soda and boiled with the luteocobaltic solution. A blue-violet coloration indicates the presence of tartaric acid. Tannic acid and paratartaric acid likewise yield a solution containing cobalt, but at the same time form a cream-coloured precipitate (C. D. Braun, *Zeitschr. anal. Chem.* 1868, p. 349).

On the distinction of tartaric from citric acid by means of permanganate solutions see CITRIC ACID (p. 472).

Martenson (*Zeitschr. f. Chem.* [2] v. 444) estimates tartaric acid as calcium tartrate, which he finds to be soluble in 2388 pts. of water, nearly insoluble in alcohol of 85 p. c., more soluble in aqueous sal-ammoniac or calcium chloride. The salt dried at 100° is dissolved in a small quantity of water in a perfectly glazed porcelain capsule, neutral solution of calcium chloride is added and a few drops of lime-water, taking care to avoid an excess, after which the liquid is stirred without touching the sides of the vessel, and left to itself for some hours. The liquid is then passed through a weighed filter, and after it has all run off, the precipitate is placed on the filter, together with a little alcohol, the liquid again allowed to run through, and the precipitate washed with alcohol, dried at 100°, and weighed as $C^4H^4CaO^6 + 4H^2O$.

Metallic Tartrates. Tartaric acid, as already observed (v. 675), is mostly bibasic, but it sometimes also exhibits the characters of a quadribasic acid, the alcoholic as well as the usually basic hydrogen-atoms being replaced by metals. The *quadribasic lead salt*, $C^4H^2\overset{''}{P}b^2O^6$, which Erdmann obtained by boiling the monoplumbic salt with aqueous ammonia, likewise separates as a crystalline powder, when neutral lead acetate is boiled for 8 to 12 hours with cream of tartar. It is quite insoluble in water, acetic acid, ammonium tartrate, and other ammoniacal salts, but dissolves easily in potash and in nitric acid. If the boiling be continued for 3 or 4 hours only, the *triplumbic salt*, $(C^4H^3O^6)^2Pb^3$, which is likewise insoluble, is obtained. A *quadribasic zinc salt*, $2C^4H^2\overset{''}{Z}n^2O^6 + H^2O$, is obtained by boiling tartaric acid with zinc and potash-solution and neutralising with nitric acid, as a powder insoluble in water, tartaric acid, and ammoniacal salts. When tartaric acid is boiled with zinc alone, the ordinary bibasic salt, $C^4H^4Zn''O^6$, separates out. The *potassium-bismuth salt*, $C^4H^2Bi'''KO^6$, prepared by Schwarzenberg (v. 686), is decomposed by water, with formation of a white, insoluble basic salt, which, when dried at 200°, has the composition $C^4H^2Bi'''KO^6 . C^4H^2Bi'''(BiO)'O^6$. *Potassio-uranic tartrate*, $C^4H^4K(UO)'O^6$ (at 200°), is obtained as an amorphous powder by boiling recently precipitated uranic hydrate with cream of tartar and evaporating the filtrate (Frisch, *J. pr. Chem.* xcvii. 278; *Jahresb.* 1866, p. 401).

According to Fleury (*Compt. rend.* lxvii. 957) the double tartrates analogous to tartar-emetic are always produced when a salt of a trioxide or sesquioxide and a salt of a monoxide are brought in contact with tartaric acid in acid or in alkaline solution. Thus when bismuth nitrate is dissolved by agitation in a solution of tartaric acid supersaturated with soda, a liquid is obtained, which, when largely diluted with water, is precipitated by salts of barium, calcium, magnesium, &c. The compounds thus formed are very slightly soluble in water, soluble in acids and in caustic soda. Analogous double salts are formed by malic and citric acid.

The optical and crystallographic characters of the acid tartrates of ammonium, thallium, rubidium, and cæsium have been examined by v. Lang (*Zeitschr. f. Chem.* [2] iii. 450). The last three form crystals belonging to the rhombic system, isomorphous with the acid tartrates of ammonium and potassium. The proportions of the axes are as follows:

	Brachy-diagonal		Macrodiagonal		Principal axis.
For $C^4H^5TlO^6$	0·6911	:	1	:	0·7186
„ $C^4H^5RbO^6$	0·6873	:	1	:	0·7010
„ $C^4H^5CsO^6$	nearly the same.				
„ $C^4H^5KO^6$ (according to Schabus) .	0·7115	:	1	:	0·7372
„ $C^4H^5(NH^4)O^6$ (acc. to De la Provostaye)	0·6983	:	1	:	0·7086

Potassium Tartrates.—According to E. Kissel (*Zeitschr. anal. Chem.* 1869, 409) 1 pt. of acid potassium tartrate dissolves in 230·1 pts. water at 10°, in 203·1 pts. at 15°, and in 152·1 pts. at 22°; 1 pt. dissolves at 12° in 318·5 pts. spirit of 6 p. c., in

360 pts. spirit of 8 p. c., in 378 pts. of 9 p. c., in 402 pts. of 10 p. c., and in 441 pts. of 12 p. c. After addition of 0·2 p. c. glacial acetic acid, spirit of 10 p. c. dissolves only 2·424 grm. of cream of tartar in a litre, the spirit alone dissolving 2·487 grm. After addition of 0·1 p. c. tartaric acid, a litre of the same spirit dissolves only 1·920 grm.

Bussy a. Buignet (*Compt. rend.* lx. 976) have examined the reaction between acid potassium tartrate and gypsum, with reference to the addition of gypsum to wines, practised in the south of France. When a solution of 2 grms. cream of tartar in 500 c.c. water containing 0·1 p. c. alcohol is digested with 0·915 grm. gypsum (equivalent proportions of the two salts), a reaction takes place represented by the equation:

$$CaSO^4.2H^2O + 2C^4H^5KO^6 = C^4H^4CaO^6 + C^4H^5KO^6 + KHSO^4 + 2H^2O,$$

the calcium appearing in the product as neutral tartrate, while the potassium remains in solution, half as acid tartrate, half as acid sulphate. Any further addition of calcium sulphate remains undecomposed, partly in the liquid, partly in the precipitate. Analogous transformations take place when gypsum is added to wine. Chancel, on the other hand (*Compt. rend.* lx. 408), supposes that *neutral* potassium sulphate and *free tartaric acid* are formed, together with the neutral calcium tartrate. He also observes that the action of the gypsum goes farther, if, instead of being added to the wine, it is added, according to general custom, to the must together with the lees. The quantities of acid potassium tartrate dissolved in 1000 pts. of pure water (I.), and of water containing 10·5 p. c. alcohol (II.), are, according to Chancel, as follows:

	0°	5°	10°	15°	20°	25°	30°	35°	40°
I.	2·44	3·00	3·70	4·53	5·53	6·70	8·05	9·60	11·30
II.	1·41	1·75	2·12	2·53	3·05	3·72	4·60	5·70	7·10

The solubility diminishes as the proportion of alcohol in the water increases; the presence of glucose, on the other hand, has no perceptible influence on it. The young and unplastered wine prepared in the south of France contains therefore from 2·5 to 3·5 grm. of cream of tartar in the litre; and as the corresponding quantity of grapes contains from 9 to 10 grm., it follows that the greater part of the acid tartrate remains in the lees. By addition of gypsum to the must, this undissolved tartar is decomposed. A saturated solution of acid potassium tartrate in water contains, after three days' digestion at 35° with excess of gypsum, 0·97 grm. tartaric acid in the litre, but when an undissolved excess of the acid tartrate is present, it contains 2·11 grm. tartaric acid in the litre. In wine thus plastered Chancel found 2·17 grm. potash in the litre; in wine fermented without gypsum, only 0·585 grm. The plastering of the must brings therefore half the tartaric acid in the must and the greater part of the potash into the wine, and, besides its clarifying action, has an important influence on the colour and durability of the wine by increasing the amount of acid in it. For Bussy a. Buignet's criticisms on Chancel's results, see *J. Pharm.* [4] i. 351; ii. 5.

Crude tartar containing a considerable quantity of yeast is apt to undergo fermentation, which diminishes the proportion of tartaric acid. A tartar containing originally 44·8 p. c. of the pure acid tartrate was found by J. Haerlin (*Dingl. pol. J.* clxxxv. 218) to contain, after 8 days' fermentation 30 p. c., after 14 days 24 p. c., and after weeks only 14·8 p. c. of pure cream of tartar. Many crude tartars contain, as roducts of decomposition, easily soluble potassium salts difficult to crystallise.

Calcium tartrate, $C^4H^4CaO^6.4H^2O$, requires for solution 6265 pts. of water at 15°, nd 352 pts. at the boiling heat (F. Mohr, *Vierteljahrs. pr. Pharm.* xiv. 428).

TARTRONIC ACID. $C^3H^4O^5$.—This acid heated with saturated aqueous ydriodic acid yields ethane and carbon dioxide, being first converted into malonic cid, $C^3H^4O^4$, which is then resolved into acetic acid and carbon dioxide, $C^3H^4O^4 +$ $= C^2H^4O^2 + CO^2$ (Berthelot).

TEA. Tea-leaves contain, according to Hlasiwetz a. Malin (*J. pr. Chem.* ci. 09), besides the constituents hitherto observed (theine, quercitannic acid, boheic id), also gallic acid, oxalic acid, and quercetin, the latter most probably existing iginally, for the greater part at least, as quercitrin. The precipitate formed in an fusion of tea by neutral lead acetate contains chiefly quercitannic, gallic, and oxalic ids; the precipitate thrown down from the filtrate by basic lead acetate contains, sides the acids just mentioned, a yellow lead-compound, which, by decomposition ith hydrogen sulphide and boiling of the filtrate with sulphuric acid, yields quercetin, $H^{18}O^{12}$, together with sugar. The presence of quercetin (or of quercitrin) in tea plains the fact that when the substances precipitable by basic lead acetate are idised with potassium hydrate, protocatechuic acid and phloroglucin are produced.

TELÆSCIN. $C^{18}H^{30}O^7$.—A product of the decomposition of æscinic acid by acids. (See HORSE-CHESTNUT, iii. 172.)

TELLURIUM. Tellurium ores (gold and silver tellurides) occur in masses in the Calaveras range between the river Stanislas and the Albany mountains in California (Mathewson, *Jahrb. Min.* 1866, p. 93). On the preparation of tellurium see H. Schwartz (*Dingl. pol. J.* clxxxvi. 29; *Jahresb.* 1867, p. 257).

TENORITE. On the crystalline form and optical characters of this mineral see Maskelyne (*Rep. 35, Br. Assoc. Notices and Abstracts*, p. 33; *Jahresb.* 1867, p. 979).

TEREPHTHALIC ACID. See PHTHALIC ACID (p. 942).

TERPILENE. See TURPENTINE OIL.

TESCHENITE. A variety of diorite occurring at Teschen and other localities in Hungary (Tschermak, *Wien. Akad. Ber.* liii. [1] 26; *Jahresb.* 1866, p. 976;—Fellener, *Jahrb. Min.* 1868, p. 207; *Jahresb.* 1867, p. 1028).

THALLIUM. Nordenskiöld (*Ann. Ch. Pharm.* cxliv. 127) has found from 16·2 to 18·5 p. c. thallium in a selenide of copper and silver from Skrikerum in Sweden, which he designates as *Crookesite*.

For the preparation of thallium from the flue-dust of pyrites burners, Wöhler (*ibid.* cxlii. 263) recommends the following process. The dust is repeatedly boiled with water acidulated with sulphuric acid; the filtered extract, not previously concentrated (otherwise arsenic would be precipitated at the same time), is mixed with hydrochloric acid, which throws down thallium chloride, and this compound, after washing with water, is converted into neutral sulphate, from the solution of which, to avoid contamination with other metals, the thallium is precipitated by electrolysis. For this purpose, a wide glass tube, tied round with bladder at the bottom, is suspended in the liquid, and filled up to the height of the thallium solution with acidulated water, and within it is fixed a plate of zinc, connected at its upper end with a platinum or copper wire immersed in the thallium solution. The thallium, which in the course of a few days is completely precipitated on the wire, is washed, with as little contact of air as possible, then pressed between paper, dried, and fused to a regulus with potassium cyanide. Carstanjen (*J. pr. Chem.* cii. 65) considers it better to knead the precipitated thallium to a solid mass under water, then hammer it into dense cubes, fuse these, previously well dried, in a porcelain crucible without the addition of any flux, and cast the metal into ingots. The small quantity of thallious oxide formed in the fusion serves to remove any metallic impurities that may be present.

Gunning (*Archives néerlandaises*, iii. 86) prepares thallium from a flue-dust consisting chiefly of arsenious and arsenic acid, together with oxides of lead and iron, by means of phosphoric acid. The dust is heated with a mixture of bone-ash, sulphuric acid, and water; the mass is strained; the residue again treated in the same manner, and the united extracts precipitated by hydrochloric acid. The filtrate containing thallium, partly as thallious chloride, partly in the form of thallic salts, is mixed with sodium sulphite; partially neutralised with sodium carbonate, and the thallium is precipitated as iodide. To prepare pure thallium salts from the crude chloride (which contains arsenic), it is best, according to Gunning, first to convert it into thallic oxide, by suspending it in a solution of sodium carbonate and passing chlorine into the liquid, taking care to keep it alkaline by adding fresh lumps of sodium carbonate if necessary. The conversion is rapid and complete. The trioxide is carefully washed, suspended in water, and reduced to thallious sulphate by passing sulphurous acid gas into the liquid. The resulting solution slowly evaporated in the air or over sulphuric acid yields pure crystals.

Oxidation.—Thallium is oxidised at ordinary temperatures by solution of potassium permanganate (Crookes, *Bull. Soc. Chim.* [2] vii. 394). When made to form the positive pole of a battery of two Bunsen's elements in water acidulated with sulphuric acid, it is converted into the black trioxide (Wöhler, *Zeitschr. f. Chem.* [2] v. 385). Paper impregnated with a thallious salt is turned brown by ozone, and was recommended by Schönbein as a delicate test for ozone. According to Laing (*ibid.* v. 416) thallium-paper may be turned brown without the action of ozone, and cannot thereby be regarded as a sure test for the latter, unless its indications are corroborated by the blueing of guaiacum-paper. With this limitation, it is a more delicate test than iodised starch-paper, and will detect ozone even in an atmosphere containing a considerable quantity of nitrous acid; it cannot however be trusted as a quantitative indicator.

Thallium Alloys. Several of these alloys have been studied by Carstanjen (*J. pr. Chem.* cii. 65; *Zeitschr. f. Chem.* [2] iv. 69), with the following results:

Alloy of :	Proportions	Solidifying Point	Colour ; Hardness
Thallium and Zinc	Equivalent proportions	above 360°	Soft like thallium. Cast bars crackle when bent
Thallium and Cadmium	"	184°	Silver-white; fine-grained; crystalline; harder than the zinc alloy
Thallium and Bismuth	"	170°	Reddish-grey; crystalline, but soft
Thallium, Cadmium, and Bismuth	6 pts. Tl, 5 pts. Bi, 1 pt. Cd	134°	Hard, brittle; recent fracture bright grey; finely granulo-crystalline
Thallium and Lead	Equivalent proportions	above 250°	Soft, non-crystalline; lead-coloured
Thallium, Lead, Bismuth	1 pt. Tl, 6 pts. Bi, 6 pts. Pb	130°	Somewhat crystalline; hard, shining
Thallium and Tin	Equivalent proportions	—	Difficult to fuse, soft, slightly ductile; does not tarnish
Thallium, Tin, Bismuth	1 pt. Tl, 2 pts. Bi, 1 pt. Sn	115°	Hard, fine-grained, light grey to white
Thallium and Copper	Equivalent proportions	Fusible only under borax at a white heat	Brass-yellow; may be cut with a knife, tarnishing on the cut surface
Thallium and Aluminium	Equivalent proportions	Do.	Tough, but softer than thallium; oxidises without burning when heated in the air
Thallium and Magnesium	Equal parts		Easily alterable; burns with magnesium flame when heated in the air

ll these alloys, except that of tin, tarnish in the air; they are more or less attacked
dilute sulphuric acid, with evolution of hydrogen.
n alloy of equal parts of thallium and *arsenic* is blackish-grey and crystalline, but
; enough to be cut with a knife. The silver-white cut surfaces acquire a blue and
ow tarnish on exposure to the air. With dilute sulphuric acid, the alloy gives off
e quantities of trihydric arsenide, and deposits a brown powder. The alloy of
lium and *antimony* in equal parts is very hard, brittle, crystalline, and has a grey
ture; with dilute sulphuric acid, it gives off trihydric antimonide. The alloys of
lium with *potassium* and *sodium* in equivalent proportions are soft and crystalline,
quesce in the air, and decompose water with violence. The sodium alloy may be
; under petroleum; the potassium alloy is altered thereby, acquiring a brown
ur. *Thallium amalgam* containing equivalent proportions of thallium and mercury

has the consistence of butter and is alterable in the air (Carstanjen). According to Nicklès (*J. Pharm.* [4] iv. 27) thallium is easily wetted and penetrated by mercury. According to J. Regnauld (*Compt. rend.* lxiv. 611) the amalgamation of thallium is attended with evolution of heat, and therefore, in accordance with a law previously established by Regnauld, the amalgam is electronegative towards the pure metal.

Chloride. A compound of thallious chloride with ferric chloride, $6TlCl.F$[illegible] is formed when recently precipitated thallious chloride is added to a concentrated solution of ferric chloride mixed with a large excess of fuming hydrochloric acid, or when thallious chloride is heated to fusion in vapour of ferric chloride. The [illegible] cinnabar-red compound is soluble in hot concentrated hydrochloric acid, and crystallises from the cooling solution in small translucent prisms permanent in the air. It is immediately decomposed by water into thallious and ferric chlorides, and can therefore be obtained in the dry state only by washing with strong hydrochloric acid, leaving it over slaked lime, and finally warming it in a current of dry carbon dioxide. The same compound is separated as a heavy red precipitate on adding a large quantity of hydrochloric acid to the liquid obtained by lixiviating the flue-dust of thalliferous iron pyrites (Wöhler, *Ann. Ch. Pharm.* cxliv. 250).

Oxides. The trioxide, or thallic oxide, is formed by the action of hydrogen dioxide on metallic thallium. The precipitate dried over sulphuric acid has the composition of the monohydrate $Tl^2O^3.H^2O$ or $Tl'''HO^2$, and becomes anhydrous when dried at 100° (Birnbaum, *Ann. Ch. Pharm.* cxviii. 133).

Thallic oxide detonates when triturated with flowers of sulphur, and slowly takes fire when triturated with 8 pts. of gold sulphide (Böttger, *Zeitschr. f. Chem.* [2] iv. [illegible]

When a rapid stream of chlorine is passed through potash-ley in which thallic oxide is suspended, the liquid acquires a deep violet-red colour, in consequence of the formation of potassium thalliate. The solution of this salt may be evaporated, diluted, and filtered through paper without decomposition; but it is reduced by oxacids to a thallious salt with rapid evolution of oxygen, by hydrochloric acid with evolution of chlorine and precipitation of thallious chloride (Carstanjen).

Oxygen-salts.—Several of these salts have been further examined by Carstanjen (*J. pr. Chem.* cii. 65, 129; *Jahresb.* 1867, p. 275); by Flemming (*Bull. Soc. Chim.* [illegible] x. 35; *Jahresb.* 1868, p. 350); and by Lang a. Descloizeaux (*Ann. Ch. Phys.* [4] [illegible] 310; *Jahresb.* 1868, p. 352). See the several Acids.

Phosphide (?). Thallium and phosphorus do not unite when fused together; neither is thallium phosphide formed by igniting the phosphate with charcoal or hydrogen (Carstanjen). Solutions of thallious salts do not act upon phosphorus; in the solution of thallious hydrate, phosphorus becomes covered with a black deposit, becoming metallically lustrous when heated, dissolving slowly in dilute hydrochloric acid (thallium ?). When phosphorus is heated with a solution of thallious hydrate in sealed tubes, a small quantity of hydrogen phosphide is evolved, and a black mass separates, whilst small whitish crystals are deposited in the tube, and phosphorous acid remains in solution (Flemming, *Jahresb.* 1868, p. 250).

Selenide. Thallium and selenium heated together in equivalent proportions unite readily without incandescence. The resulting compound, Tl^2Se, is black, easily fusible; in the solid state it is scoriaceous and vesicular, hard, brittle, and changes colour on exposure to the air. It is not attacked by water, and dilute sulphuric acid attacks it only when heated, dissolving it slowly with evolution of hydrogen selenide. When the quantity of selenide used is between 1 and 3 eq. the product crystallises on cooling in radiating prisms which are permanent in the air, resist the action of dilute sulphuric acid, and are attacked by the concentrated acid only when heated, sulphurous oxide being then evolved. A definite triselenide does not appear to be producible in the dry way (Carstanjen).

Sulphides. Thallium forms a monosulphide, a trisulphide, and intermediate sulphides. The *monosulphide*, Tl^2S, is formed by precipitation of neutral thallious salts with hydrogen sulphide or ammonium sulphide (v. 756), also by fusing 204 pts. thallium with 16 pts. sulphur at the heat of a blast furnace. It is then obtained as a black, shining, brittle mass having a crystalline structure. The *trisulphide*, Tl^2S^3, obtained by fusing 2 at. thallium with more than 3 at. sulphur, and volatilising the excess of sulphur without contact of air, is black, easily fusible, soft, and ropy at summer temperature; brittle, with vitreous fracture, below 12°. It is attacked by dilute sulphuric acid when heated, and dissolved without separation of sulphur; neither does it give up sulphur to carbon bisulphide. Fused with the monosulphide, it yields an intermediate sulphide crystallising in grey-black prisms. Intermediate crystallisable thallium sulphides of variable composition are likewise produced by precipitating the so-called sesquichloride (v. 747) with ammonium sulphide, or by fusing 2 at. thallium with more than one and less than three atoms of sulphur; two such sulphides xhibited the composition $Tl^2S.Tl^2S^3$ and $5Tl^2S.3Tl^2S^3$. They do not yield any sulphur carbon bisulphide, but give up part of their sulphur (as also does the trisulphide) hen heated in an open glass tube. All the sulphides of thallium are decomposed by nition in a stream of hydrogen (Carstanjen).

Thallium sulpharsenate is formed as a reddish-yellow precipitate when hydrogen lphide is passed into a neutral or acid solution of a thallious salt mixed with senious acid, or when an ammoniacal solution of arsenious sulphide is mixed with e ammoniacal solution of a thallious salt. When precipitated from acid solutions ntaining excess of thallium, it has the composition $Tl^2S.As^2S^3$. A similar precipite is formed when hydrogen sulphide is passed into crude thallium chloride prepared om arsenical flue-dust, or into the crude aqueous extract of such flue-dust. When a lution containing arsenious acid and thallious sulphate in the proportion to form the lpharsenite is treated with hydrogen sulphide, the whole of the arsenic is precipited, but not all the thallium, a portion of that metal remaining in solution even when e arsenic is in considerable excess. On adding more arsenious acid a fresh precipite containing thallium is formed, and by continuing this treatment the whole of the allium may ultimately be precipitated. All the precipitates formed as above have e same colour (Gunning, *Archives néerlandaises*, iii. 86; *Jahresb.* 1868, p. 249).

THEOBROMINE. A solution of this base in strong hydrochloric acid mixed th potassium iodide and left to itself, deposits large nearly black prisms consisting of e periodide $C^7H^8N^4O^2HI^4$; this compound is decomposed even by heating with alcohol örgensen, *Zeitschr. f. Chem.* [2] v. 675).

THERMO-CHEMISTRY. Further determinations of the heat of neutralisan of acids and bases have lately been published by Thomsen (*Pogg. Ann.* cxliii. 4–396 and 497–534; *Deut. chem. Ges. Ber.* iv. 586).

The following tables give the numbers of thermal units (gramme-degrees) evolved en one molecule of hydrogen sulphate, H^2SO^4, or an equivalent quantity of another id, diluted with 400 molecules of water, is neutralised by an equivalent quantity of se in the same state of dilution:

TABLE I.

R	Sulphuric acid ($R.H^2SO^4.Aq$)	Hydrochloric acid ($R.2HCl.Aq$)	Nitric acid ($R.2HNO^3.Aq$)	Acetic acid ($R.2C^2H^4O^2.Aq$)
$2LiHO.Aq$	31290	27700	—	—
$2NaHO.Aq$	31380	27490	27360	26370
$2KHO.Aq$	31290	27500	27540	26430
$2TlHO.Aq$	31130	44340*	—	—
$2N(C^2H^5)^4.Aq$	31010	—	—	—
$BaH^2O^2.Aq$	36900*	27780	28260	26900
$SrH^2O^2.Aq$	30710	27630	—	—
$CaH^2O^2.Aq$	31140	27900	—	—
MgH^2O^2	31220	27690	27520	—
$2(NH^4.HO)$	28150	24540	24640	—
$2[N(C^2H^5)^3H.HO]$	28340	25040	—	—
MnH^2O^2	26480	22950	—	—
NiH^2O^2	26110	22580	—	—
CoH^2O^2	24670	21140	—	—
FeH^2O^2	24920	21390	—	—
CdH^2O^2	23820	20290	20320	—
ZnH^2O^2	23410	19880	—	18030
CuH^2O^2	18440	14910	14890	12820
PbH^2O^2	21060*	14360*	15340	13120
CuO	18800	15270	15250	13180
HgO	—	19420	—	—
PbO	23500*	16790*	17770	15460
Ag^2O	14490	42380*	10880	—
AlH^3O^3	20990	18640	—	—
BeH^3O^3	16100	13640	—	—
CrH^3O^3	16440	13730	—	—
AuH^3O^3	—	13680	—	—
FeH^3O^3	11250	11150	11200	7990

In the cases marked by the asterisk, the salt formed is insoluble, or almost insoluble, so that r the whole or part of the heat of neutralisation has to be added to the heat of precipitation.

water-bath. Acetosalicylol then remains in the form of an oil which soon solidifies to a crystalline mass; its formation is represented by the equation:

$$C^6H^4\left\{\begin{matrix}ONa\\COH\end{matrix}\right. + (C^2H^3O)^2O = C^2H^3O(ONa) + C^6H^4\left\{\begin{matrix}OC^2H^3O\\COH\end{matrix}\right..$$

Acetyl-salicylol melts at 37°, and resolidifies to a satiny crystalline mass; boils at about 253°, and distils with slight decomposition. It dissolves easily in ether and in alcohol, and crystallises therefrom in silky needles; the solutions do not colour ferric chloride purple. By *potash* it is resolved into potassium acetate and potassium salicylol:

$$C^6H^4\left\{\begin{matrix}OC^2H^3O\\COH\end{matrix}\right. + 2HOK = C^2H^3O(OK) + C^6H^4\left\{\begin{matrix}OK\\COH\end{matrix}\right. + H^2O,$$

whereas coumaric acid similarly treated yields acetate and salicylate of potassium, with evolution of hydrogen:

$$C^6H^4\left\{\begin{matrix}C^2H^3O\\COOH\end{matrix}\right. + 2HOK = C^2H^3O(OK) + C^6H^4\left\{\begin{matrix}OH\\CO^2K\end{matrix}\right. + H^2.$$

Acetyl-salicylol is decomposed by boiling with *water*. It unites with *acetic anhydride* when the two are heated together to 150°, forming a crystalline compound, $C^9H^8O^3.C^4H^6O^3$, analogous to that of salicylol (p. 1000). This compound melts at 100°–101°, decomposes when distilled, and separates from solution in acetic anhydride in oblique four-sided tables. It is soluble in ether, carbon tetrachloride, and benzol, easily soluble in hot, sparingly in cold alcohol. By water at 150° it is completely resolved into acetic acid and salicylol.

If instead of adding acetic anhydride to sodium salicylol suspended in ether, and decanting from the sodium acetate as above described, the sodium salicylol be dissolved in acetic anhydride, the solution boiled for a few minutes, and then poured into water, an oily body separates, while sodium acetate remains in solution. On distilling this oil, acetic anhydride passes over first, then salicylol, and finally at 290° coumarin, $C^9H^6O^2$, which crystallises in the receiver. This compound results from dehydration of acetyl-salicylol formed in the first instance: $C^9H^8O^3 - H^2O = C^9H^6O^2$; and its formation appears to depend upon the presence of sodium acetate, inasmuch as acetic anhydride alone produces only acetyl-salicylol. Perhaps the anhydro-acetate, $C^2H^3O^2Na.C^4H^6O^3$ (which Perkin has obtained in needle-shaped crystals by dissolving sodium acetate in acetic anhydride), plays some unexplained part in this reaction.

Butyric coumarin, $C^{11}H^{10}O^2$, and *valeric coumarin*, $C^{12}H^{12}O^2$, are obtained in like manner by the action of butyric and valeric anhydrides on sodium-salicylol (p. 500).

Butyryl-salicylol. $C^{11}H^{12}O^3 = C^6H^4\left\{\begin{matrix}OC^4H^7O\\COH\end{matrix}\right.$ (Perkin, *Chem. Soc. J.* [2] vi. 472).—Prepared by leaving an ethereal solution of butyric anhydride in contact with sodium-salicylol for two or three days, then decanting from the sodium-butyrate, and proceeding as in the preparation of the preceding compound. It distils between 260° and 270°, as an oil smelling like butyric acid and salicylol. It is quickly decomposed by strong *potash-solution*, yielding potassium butyrate and potassium salicylol. On heating it to 140°–150° with *acetic anhydride*, and leaving the slightly brown mass in contact with water for two days, crystals are obtained having the composition $C^{13}H^{14}O^6$, and identical with the above-described compound of acetosalicylol with acetic anhydride; an interchange of the radicles acetyl and butyryl must therefore have taken place.

When a mixture of butyrosalicylol, butyric anhydride, and sodium butyrate is heated to boiling for a short time in an open vessel, then washed with water and distilled, the last third of the distillate solidifies on cooling, and when recrystallised from alcohol, yields pure butyric coumarin, $C^{11}H^{10}O^2 = C^{11}H^{12}O^3 - H^2O$; and this compound boiled with potash is converted into butyro-coumaric acid, $C^6H^4\left\{\begin{matrix}C^4H^7O\\COOH\end{matrix}\right.$, isomeric with butyrosalicylol. (See COUMARIN and COUMARIC ACID, pp. 500, 501.)

Benzoyl-salicylol. $C^{14}H^{10}O^3 = C^6H^4\left\{\begin{matrix}OC^7H^5O\\COH\end{matrix}\right.$ (Perkin, *Laboratory*, i. 51; *Zeitschr. f. Chem.* 1867, p. 346).—Produced by the action of benzoyl chloride on sodium-salicylol, and separates on treating the product with water, as a thick oil, which distils at a temperature above the range of the mercurial thermometer. It forms a white pulverulent compound with acid sodium sulphite, and crystalline compounds with the acid sulphites of potassium and sodium. Heated with alcoholic potash it yields benzoic acid and salicylol; with alcoholic ammonia it forms a brown viscid product, together with a crystalline body.

THIOCHRONIC ACID. See QUINONES (p 990).

THIONESSAL. $C^{28}H^{20}S$.—This compound, discovered by Laurent, who assigned to it the formula $C^{28}H^{18}S$ (v. 779), has been further examined by Fleischer (*Ann. Ch. Pharm.* cxliv. 192), and by Dorn (*Zeitschr. f. Chem.* [2] v. 597). It is produced by dry distillation of thiobenzene, benzyl sulphide, benzyl disulphide, or sulphobenzide. When benzyl sulphide, $(C^7H^7)^2S$, is distilled, toluene and benzyl sulphydrate pass over at first, then toluylene (stilbene), and lastly, at a very high temperature, tolallyl sulphide and thionessal. The distillate may be freed from a yellow oil and tolallyl sulphide, by treatment with a large quantity of ether, and the thionessal, which remains undissolved, crystallised from boiling alcohol. Thionessal crystallises in small white needles melting at 180°; it is not altered either by melting potassium hydrate or by heating with sodium (Fleischer).

Tribromothionessal, $C^{28}H^{17}Br^3S$, is formed on adding bromine to thionessal suspended in water, as a yellowish granular powder, which, after washing with hot alcohol and ether, crystallises from petroleum of high boiling point in hard microscopic needles. It melts at 265°-270°, is not attacked by alcoholic potash or by benzene and sodium at the boiling heat, but is decomposed by fusion with sodium. By further treatment with bromine it is converted into *tetrabromothionessal*, $C^{28}H^{16}Br^4S$, which is quite insoluble in alcohol, ether, and petroleum (Fleischer).

Thionessal heated to 130°-140° with 2 mol. phosphorus pentachloride, is decomosed according to the equation:

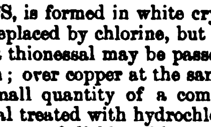
$$C^{28}H^{20}S + 2PCl^5 = PSCl^3 + PCl^3 + 4C^7H^5Cl,$$

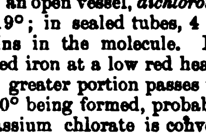
orming an oily compound which solidifies with water, dissolves sparingly in alcohol, asily in hot ether or benzol, and separates therefrom in needles melting at 130°-132°. This body, C^7H^5Cl, or a multiple thereof, is not altered by heating with water or lcoholic ammonia to 180°, or by heating with benzol and sodium (Fleischer). According to Dorn, on the other hand, thionessal is not desulphurised by phosphorus entachloride. When the two are heated together in an open vessel, *dichlorothionessal*, $C^{28}H^{18}Cl^2S$, is formed in white crystals melting at 219°; in sealed tubes, 4 at. hydroen are replaced by chlorine, but the sulphur remains in the molecule. Dorn also nds that thionessal may be passed over finely divided iron at a low red heat without lteration; over copper at the same temperature the greater portion passes unaltered, nly a small quantity of a compound melting at 60° being formed, probably tolane. hionessal treated with hydrochloric acid and potassium chlorate is converted into xylepidene, and dichlorothionessal in like manner into dichloroxylepidene (Dorn).

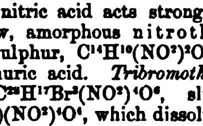
Fuming nitric acid acts strongly on thionessal, producing, in the first instance, ght yellow, amorphous nitrothionessal, $C^{28}H^{16}(NO^2)^4S$, then a nitro-compound ce from sulphur, $C^{14}H^{10}(NO^2)^2O^2$, and lastly paranitrobenzoic acid together ith sulphuric acid. *Tribromothionessal* treated with nitric acid yields a yellow wder, $C^{28}H^{17}Br^3(NO^2)^4O^6$, slightly soluble in hot alcohol, and an acid, $^{28}H^{17}(Br^3)(NO^2)^4O^4$, which dissolves easily in alcohol and ether, melts at 180°, and rms a barium salt, $C^{28}H^{12}Ba^2Br^4(NO^2)^4O^4 + 8H^2O$, crystallising in yellowish dules. Thionessal dissolves in fuming sulphuric acid at ordinary temperatures, d in ordinary sulphuric acid when heated, forming a deliquescent acid, $C^7H^6SO^4$, ich crystallises from alcohol in laminæ or tufts of needles, and yields a barium lt, $(C^7H^5SO^4)^2Ba + 4H^2O$, crystallising in hard crusts, and a zinc salt, $(C^7H^5SO^4)^2Zn$ ystallising in deliquescent needles or laminæ. When vapour of thionessal is passed er red-hot soda-lime, tolallyl sulphide collects in the receiver in the form of a yellow wder (Fleischer).

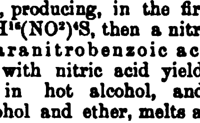
Thionessal and tolallyl sulphide are the sulphur-compounds analogous to lepiden d oxylepidene (p. 780).

Dorn represents these four compounds by the following constitutional formulæ:


Thionessal.


Lepidene.


Tolallyl su'phide.


Oxylepidine.

THIOSINAMINE. $C^4H^8N^2S = N^2(CS)''(C^3H^5)H^2$. *Allylsulphocarbamide* (v. 781).—Several new derivatives of this compound have been obtained by Maly (*Zeitschr. f: Chem.* [2] v. 258).

Thiosinamine Iodide, $C^4H^8N^2SI^2$, is formed, like the bromide (v. 782), by direct combination of iodine with thiosinamine in alcoholic solution. It is soluble in water and in alcohol, and separates from the latter in brittle, nearly colourless groups of crystals; begins to melt and decompose at 90°; and at a higher temperature gives off violet vapours, afterwards products having the odour of allyl compounds, and at a higher temperature volatilises completely. Strong sulphuric acid colours the solution violet and eliminates hydriodic acid; strong nitric acid separates the iodine as a black powder. Silver nitrate removes all the iodine, but recently precipitated silver chloride takes away only 1 at. iodine, replacing it by chlorine, and forming *thiosinamine iodochloride*, $C^4H^8N^2SICl$, which separates from alcohol in colourless crystals, easily soluble in water and alcohol, melting to a yellow liquid and decomposing at a higher temperature. By treating the aqueous solution of the di-iodide with silver cyanide, and evaporating the filtered liquid, a compound of *thiosinamine iodocyanide* with *silver cyanide* is obtained, as a heavy whitish-yellow powder, which when once separated from the liquid is insoluble in water, alcohol, ether, and ammonia. It is decomposed by strong sulphuric acid, and when heated, swells up in snake-like forms, like the sulphocyanates of mercury.

Thiosinamine Ethyliodide, $C^4H^8N^2S.C^2H^5I$, is obtained by dissolving equivalent quantities of thiosinamine and ethyl iodide, and leaving the solution to evaporate till it becomes syrupy. It then separates in large, colourless, transparent, well-defined crystals, which dissolve in all proportions of water, very easily in alcohol and ether, and decompose at 72°. Silver solution removes all the iodine. The corresponding *amyl-compound*, $C^4H^8N^2S.C^5H^{11}I$, forms large, colourless, deliquescent crystals. Benzoyl chloride appears to form a similar compound with thiosinamine.

Thiosinamine Dicyanide, $C^4H^8N^2S.(CN)^2$, prepared by passing cyanogen gas into an alcoholic solution of thiosinamine, and purified by repeated crystallisation from hot alcohol, forms a loose network of shining, golden-yellow, crystalline laminæ, moderately soluble in boiling alcohol, very slightly in benzol and ether, insoluble in water. The yellow alcoholic solution does not yield silver cyanide when boiled with silver oxide. The compound dissolves easily in potash, giving off ammonia when heated, and forming a faintly yellowish solution, with light green fluorescence.

Oxalyl-thiosinamine, $C^6H^6N^2SO^2 = N^2(CS)''(C^2O^2)''(C^3H^5)H$, is formed by dissolving thiosinamine dicyanide in warm dilute sulphuric acid, and separates on cooling in large groups of lemon-yellow needles, the mother-liquor retaining a portion of it, together with ammonium-sulphate:

$$C^4H^8N^2S(CN)^2 + H^2SO^4 + 2H^2O = (NH^4)^2SO^4 + C^6H^6N^2SO^2.$$

Oxalyl-thiosinamine is moderately soluble in cold, easily in hot water, very soluble in alcohol and ether. It melts at 80°–90°, and burns with flame on platinum foil. The aqueous solution has a distinct acid reaction, is not clouded by barium chloride, but gives with silver nitrate, lead acetate, and baryta-water, precipitates which quickly decompose. The solution is decolorised by strong nitric acid, and then gives the reaction of that acid. With zinc and dilute sulphuric acid it becomes decolorised and gives off hydrogen sulphide. Strong sulphuric acid dissolves it with orange-red colour; potash does not perceptibly alter it. By baryta-water it is resolved into thiosinamine and oxalic acid: $C^6H^6N^2SO^2 + BaH^2O^2 = BaC^2O^4 + C^4H^8N^2S$. With silver nitrate in aqueous solution it yields silver sulphide and a silver compound of oxalyl-allyl urea, $N^2(CO)(C^2O^2)(C^3H^5)H$, which crystallises in groups of white silky needles. If the oxalyl-thiosinamine be boiled with excess of silver nitrate, silver oxalate and allyl urea are produced.

Phenyl-thiosinamine, $C^4H^7(C^6H^5)N^2S$ (v. 783), unites with iodine like thiosinamine, but the compound does not crystallise. Bromine, on the other hand, decomposes phenyl-thiosinamine. *Phenyl-thiosinamine dicyanide*, $C^{10}H^{12}N^2S.(CN)^2$, is formed by passing cyanogen gas into an alcoholic solution of phenyl-thiosinamine, and may be obtained, by precipitation with water and recrystallisation from alcohol, as a mass of crystals grouped in stellate forms; but it is not easily purified from adhering phenyl-thiosinamine. When its alcoholic solution is heated with dilute sulphuric acid, the entire liquid solidifies to a mass of long, very slender needles of oxalyl-phenyl-thiosinamine:

$$\underset{\text{Phenyl-thiosinamine dicyanide.}}{N^2(CS)(C^3H^5)(C^6H^5)H^2.(CN)^2} + H^2SO^4 + 2H^2O = (NH^4)^2SO^4 +$$

$$\underset{\text{Oxalyl-phenyl-thiosinamine.}}{N^2(CS)(C^2O^2)(C^3H^5)(C^6H^5)}$$

This compound is insoluble in water, slightly soluble in cold alcohol, very easily in hot alcohol and benzol, soluble also in ether and in amyl alcohol. It is decolorised by hot nitric acid, but without formation of sulphuric acid; dissolves readily in strong sulphuric acid, and is precipitated by water, apparently unaltered. It melts at 161° to a clear yellow liquid, and solidifies on cooling to a radio-crystalline mass. Treated in hot alcoholic solution with baryta-water, it is resolved into oxalic acid and phenyl-thiosinamine. The warm alcoholic solution forms with silver nitrate a precipitate of silver sulphide and a solution of *oxalyl-phenyl-allyl-carbamide*, $N^2(CO)(C^2O^2)(C^3H^5)(C^6H^5)$, the reaction consisting in a simple interchange of sulphur and oxygen. Oxalyl-phenyl-allyl-carbamide is insoluble, but dissolves easily in strong alcohol, benzol, carbon bisulphide, and warm amyl alcohol; melts at 108°; is not precipitated by metallic salts; dissolves in strong sulphuric and in strong nitric acid, and is reprecipitated by water. By baryta-water it is resolved into oxalic acid and phenyl-allyl-carbamide, $N^2(CO)(C^3H^5)(C^6H^5)H^2$, which crystallises in shining white needles melting at 96°–97°.

Tolyl-thiosinamine, $C^{11}H^{14}N^2S = C^4H^7(C^7H^7)N^2S$, first obtained by Jaillard (v. 874), is more easily prepared by mixing an alcoholic solution of toluidine with oil of mustard. The liquid solidifies after a while to a crystalline pulp containing tolyl-thiosinamine and another compound, which may be easily separated by hot alcohol, in which the former dissolves very easily, the latter with difficulty. Tolyl-thiosinamine separates from the alcoholic solution, on cooling, in soft white crystalline masses, consisting when dried of unctuous laminæ. It melts at 97° (at 112° according to Jaillard).

Oxalyl-tolyl-thiosinamine, $C^{13}H^{12}N^2SO^2 = N^2(CS)''(C^2O^2)''(C^3H^5)(C^7H^7)$, is produced by saturating an alcoholic solution of tolyl-thiosinamine with cyanogen gas, and heating it after a while with dilute sulphuric acid. The liquid on cooling solidifies to a mass of yellow needles, which when washed with alcohol and water, and recrystallised from hot alcohol, yields oxalyl-tolyl-thiosinamine in long golden-yellow, rather narrow, and very flat needles, having a metallic lustre. It dissolves easily in hot, slightly in cold alcohol, forming a neutral solution; is insoluble in water, but soluble in ether, benzol, nethyl alcohol, amyl alcohol, and carbon bisulphide. It melts at 157° to a deep yellow liquid, which soon solidifies to a crystalline mass; may be sublimed completely and without decomposition in a glass tube. Strong sulphuric acid dissolves t to a yellow liquid, from which it appears to be precipitated by water in its original tate. Silver nitrate forms in the alcoholic solution a precipitate of silver sulphide; uric chloride forms a precipitate having the colour of ferric oxide; platinic chloride orms no precipitate. Hot strong nitric acid dissolves oxalyl-tolyl-thiosinamine ithout alteration. Baryta-water decomposes it into oxalic acid and tolyl-thiosinamine Maly).

THOMSONITE. A mineral from Iceland having the optical properties of omsonite (faroelite) was found by F. v. Kobell (*J. pr. Chem.* xcviii. 134; *Jahresb.* 866, p. 940) to contain 41·00 p. c. SiO^2, 31·66 Al^2O^3, 4·50 Na^2O, and 12·11 water, ading to the formula $2Na^2O.3SiO^2 + 3(2CaO.SiO^2) + 5(2Al^2O^3.3SiO^2) + 10H^2O$.

THYMOL. $C^{10}H^{14}O$. *Cymylic Phenol.*—Of this homologue of phenol there are ro modifications, viz. α thymol, existing in the volatile oils of thyme, horse-mint, id *Ptychotis Ajowan* (v. 793); and β thymol, produced by fusing the potassium salt cymyl-sulphurous or sulphocymolic acid with sodium hydrate, dissolving the fused ass in water, acidulating with sulphuric acid, and distilling in a current of steam; then passes over as a yellowish viscid oil, lighter than water, which cannot be lidified either by cooling or by contact with a crystal of α thymol (R. Pott, *Zeitschr. Chem.* [2] v. 201;—H. Müller, *ibid.* 284).—α Thymol dissolves easily and comotely in strong sulphuric acid at 40°–50°, and the solution does not become turbid dilution with water, because the thymol has been converted into an easily soluble lpho-acid. β Thymol likewise dissolves easily in strong sulphuric acid, but only a iall portion of it is thereby converted into a sulpho-acid even at 100°, and on dition of water, the greater part of the oil separates out unaltered. The aqueous lution neutralised with barium carbonate yields a barium salt, $(C^{10}H^{13}SO^4)^2Ba$, ich crystallises in anhydrous needles. β Thymol dissolves easily in alkalis, and is ecipitated therefrom by acids (Pott).

α Thymol heated with phosphoric anhydride is very easily and completely resolved o propylene and γ cresol (p. 507), the latter remaining in combination with phosoric acid. α Thymol is therefore propyl-cresol, that is to say, propyl-methyl-phenol, $I^3(OH)\left\{\begin{matrix}C^3H^7\\ C\,H^3\end{matrix}\right.$ (Engelhardt a. Latschinoff, *Zeitschr. f. Chem.* [2] v. 616); and as nene is propyl-methyl-benzene, it follows also that β thymol has the constitution of propyl-methyl-phenol (Pott). Probably one modification contains normal propyl and the other isopropyl.

DERIVATIVES OF *a* THYMOL (Engelhardt a. Latschinoff, *Zeitschr. f. Chem.* [2] v. 43).

Methyl-thymol, $C^{10}H^{13}O(CH^3)$, is obtained by heating an alcoholic solution of equal quantities of thymol and potassium hydrate with excess of methyl iodide:

$$C^{10}H^{13}OH + KHO + CH^3I = KI + H^2O + C^{10}H^{13}O(CH^3).$$

Precipitated from the alcoholic solution by water, treated with potash, and rectified, it forms an oily liquid having an aromatic odour and burning taste, boiling at [illegible] insoluble in water, easily soluble in alcohol and ether. Sp. gr. = 0·941 at 18°.

Ethyl-thymol, $C^{10}H^{13}O(C^2H^5)$, is obtained by heating sodium-thymol in a sealed tube with ethyl iodide (Jungfleisch, *Bull. Soc. Chim.* [2] iv. 17), or by boiling an alcoholic solution of thymol and potassium hydrate with ethyl iodide (Engelhardt a. Latschinoff). It is a colourless mobile liquid having an aromatic odour, like that of carrots, and an extremely burning taste; insoluble in water, easily soluble in alcohol and ether; boils without decomposition at 222°; oxidises slowly in the air. Potash does not attack it even when heated. With strong sulphuric acid it forms a soluble compound, probably analogous to that which is formed under similar circumstances from anisol (Jungfleisch).

Amyl-thymol, $C^{10}H^{13}O(C^5H^{11})$, obtained like the preceding, is an oily liquid insoluble in water, boiling with partial decomposition at 238°–243°.

Benzoyl-thymol, $C^{10}H^{13}O(C^7H^5O)$, is formed by heating thymol with benzoyl chloride. After washing with soda-ley, &c., it forms an oil which distils without decomposition, does not become solid in a freezing mixture, but after keeping for some time solidifies to a crystalline mass which melts at the heat of the hand. It is soluble in ether, and when heated with ordinary sulphuric acid, is resolved into benzoic acid and *a* sulphothymolic acid.

Cymylene-thymol. $(C^{10}H^{13}O)^2(C^{10}H^{12})''$. *Cumol-thymol.*—When 2 mol. thymol are heated with 2 mol. potassium hydrate and 1 mol. cymylene chloride, $C^{10}H^{12}Cl^2$ (prepared by the action of phosphorus pentachloride on cuminic aldehyde), potassium chloride separates, and the alcoholic solution mixed with water yields an oil, which is insoluble in potash, and solidifies after a while to a crystalline mass. Cymylene-thymol crystallises in rhombic tables melting at 157°.

When an alcoholic solution of 3 mol. thymol and 3 mol. potassium hydrate is boiled with 1 mol. *chloroform*, potassium chloride is formed, and the alcoholic filtrate mixed with water deposits a brown oil. *Benzotrichloride*, $C^7H^5Cl^3$, treated in the manner with potash and thymol, yields analogous products. The brown oil separated by water is resolved by heating with sulphuric acid into benzoic acid and *a* sulphothymolic acid.

Thymol Phosphate, $(C^{10}H^{13}O)^3(PO)'''$, is formed by heating thymol with phosphorus oxychloride: $3C^{10}H^{13}OH + POCl^3 = 3HCl + (C^{10}H^{13}O)^3PO$, and may be separated—by treating the product with potash, dissolving in ether, drying with calcium chloride, evaporating the ether, and heating the residual liquid to 200°—as a brownish oil which solidifies after some time to a crystalline mass. Thymol phosphate is likewise produced by heating 4 mol. thymol with 1 mol. phosphorus pentachloride. It is insoluble in water, easily soluble in ether and alcohol, and separates from solution in absolute alcohol by slow evaporation, in large translucent prisms having a fatty lustre. From an ethereal solution it crystallises in flat needles. It melts at 59°.

Sulphothymolic Acids. $C^{10}H^{14}SO^4 = C^{10}H^{12}\left\{\begin{matrix}OH\\SO^3H\end{matrix}\right.$. *Thymylsulphuric* or *Cymylsulphuric Acids.*—By treating thymol with sulphuric acid, Lallemand obtained a sulphothymolic acid which yielded soluble and well-crystallised barium and lead salts. Engelhardt a. Latschinoff have further examined the products of this reaction, and have obtained three isomeric sulphothymolic acids, which they distinguish by the prefixes *a*, *β*, *γ*; also a disulphothymolic acid, $C^{10}H^{12}(SO^3H)^2$.

a Sulphothymolic acid is the chief product of the action of ordinary sulphuric acid on thymol at comparatively low temperatures, and is obtained quite pure, without the slightest admixture of the *β* and *γ* acids, by gradually adding sulphuric chlorhydrate, SO^2HCl, to thymol. Hydrochloric acid is then evolved, and the liquid on cooling solidifies to a crystalline mass of pure *a* sulphothymolic acid. A mixture of 60 grms. thymol and 40 grms. ordinary sulphuric acid, if left in a warm place (at about 50°), gradually becomes solid; and on dissolving the crystalline mass in water, filtering from unaltered thymol, agitating with ether, neutralising with barium carbonate, and evaporating, a large quantity of barium *a* sulphothymolate separates in fine crystals. The last mother-liquors yield, together with crystals of the α salt, sparingly soluble laminæ of totally different character; and by dissolving these crystals together with the mother-liquor in water, converting the dissolved barium salt into a potassium salt, and concentrating the aqueous solution, sparingly soluble laminæ are obtained, consisting of the potassium salt of β sulphothymolic acid. On evaporating the mother-liquor of the first crystallisation to dryness, and dissolving the dry mass in boiling alcohol of 90 p. c., the alcoholic solution first yields on cooling, needles of the potassium salt of disulphothymolic acid, which is sparingly soluble in alcohol, and the mother-liquor of these needles yields by evaporation the easily soluble potassium salt of α sulphothymolic acid. The principal product of the reaction is α sulphothymolic acid, the β acid and disulphothymolic acid being obtained only in very small quantities.

The α *sulphothymolates* are easily soluble in water, and are coloured dark violet by ferric chloride. The *potassium salt*, $C^{10}H^{12}(OH)(SO^3K) + 2\frac{1}{2}H^2O$, crystallises from very concentrated aqueous solutions in beautiful transparent rhombic tables, or large prisms; from boiling alcohol, in which it is also very soluble, in large rhombic tables; the crystals effloresce in the air. The *barium salt*, $(C^{10}H^{13}SO^4)^2Ba + 4H^2O$, crystallises in flat transparent prisms decomposing at 100°. The *lead salt*, $(C^{10}H^{13}SO^4)^2Pb + 4H^2O$, crystallises from very strong aqueous solutions in stellate groups of needles; it is very soluble in boiling alcohol, and the solution solidifies on cooling to a mass of slender needles; the salt decomposes at 110°. The *copper salt* separates from alcoholic solution in indistinct crystalline crusts.

β *Sulphothymolic acid* is especially characterised by the sparing solubility of its potassium salt, $C^{10}H^{13}SO^4K + H^2O$, which crystallises from boiling aqueous solution in thin plates, and decomposes when heated above 115°. Its solution is coloured violet-blue by ferric chloride.

γ *Sulphothymolic acid*, $C^{10}H^{14}SO^4$, is produced, together with disulphothymolic acid, by heating thymol with a mixture of ordinary and fuming sulphuric acids, neutralising with barium carbonate, converting the resulting barium salts into potassium salts, and separating these salts by crystallisation from boiling alcohol, the disulphothymolate crystallising out first as the solution cools, and the mother-liquor yielding by evaporation granular masses of the γ sulphothymolate. This salt, $C^{10}H^{13}SO^4K + H^2O$, is very soluble in water and alcohol; does not decompose at 135°. The *barium salt*, $(C^{10}H^{13}SO^4)^2Ba + 3H^2O$, is more soluble in water than the α-sulphothymolate, and crystallises therefrom in tufts of needles; does not decompose at 135°.

Potassium Disulphothymolate, $C^{10}H^{11}(OH)(SO^3K)^2 + 1\frac{1}{2}H^2O$, is very soluble in water, sparingly soluble in cold, more easily in boiling alcohol, and crystallises from the boiling alcoholic solution in long slender shining needles which on exposure to the air mmediately crumble to a white powder.

Methyl-sulphothymolic acid, $C^{11}H^{16}SO^4 = C^{10}H^{12}\left\{\begin{matrix}OCH^3\\SO^3H\end{matrix}\right.$, is obtained by the ction of sulphuric acid on methyl-thymol. Its barium salt, $(C^{11}H^{15}SO^4)^2Ba + 3H^2O$, s very soluble in boiling water, and crystallises in small nodules on cooling.

Ethyl-sulphothymolic Acid. $C^{12}H^{18}SO^4 = C^{10}H^{12}\left\{\begin{matrix}OC^2H^5\\SO^3H\end{matrix}\right.$.—Of this acid there re two modifications, α and γ, obtained by the action of ethyl iodide on the salts of he corresponding sulphothymolic acids. The potassium salts of the two acids have ıe same composition, $C^{10}H^{12}(OC^2H^5)(SO^3K)$. The α salt crystallises in thin tables, ıe γ salt in flat needles; both dissolve sparingly in cold, easily in boiling water, and esemble each other closely in other respects; so likewise do all the other correspondg salts of the two acids. The solutions of the potassium salts mixed with barium loride yield precipitates of the barium salts, which crystallise from boiling water, ıe α salt in thin laminæ, the γ salt in six-sided tables, both containing $(C^{12}H^{17}SO^4)^2Ba$ 3H²O. Ethyl-thymol dissolves when heated with ordinary sulphuric acid, and by utralising the solution with barium carbonate, two salts are obtained, the less luble of which is the α ethyl-sulphothymolate, while the more soluble is not isomeric ith it.

α *Amyl-sulphothymolic acid*, $C^{15}H^{24}SO^4 = C^{10}H^{12}\left\{\begin{matrix}OC^5H^{11}\\SO^3H\end{matrix}\right.$, is obtained by ating the potassium salt of α sulphothymolic acid with potash and amyl-iodide. ıe *potassium salt*. $C^{15}H^{23}SO^4K$, crystallises in needles easily soluble in water. The *rium salt*, $(C^{15}H^{23}SO^4)^2Ba + 3H^2O$, forms flat needles sparingly soluble in cold, more sily in boiling water. By dissolving amyl-thymol in warm sulphuric acid, neutralng with barium carbonate, and evaporating, flat needles of the same salt are obtained, d the mother-liquor yields a more soluble salt having the same composition.

α *Benzoyl-sulphothymolic Acid.* $C^{17}H^{18}SO^{5} = C^{10}H^{12}\left\{\begin{matrix}OC^{7}H^{5}O\\SO^{3}H\end{matrix}\right.$.—The potassium salt of this acid, $C^{17}H^{17}SO^{5}K + 2H^{2}O$, is obtained by heating the α sulphothymolate to 125° with benzoyl chloride. It is slightly soluble in cold, more soluble in boiling water, and crystallises on cooling in flat shining needles. The other α benzoyl-sulphothymolates are also slightly soluble in cold, more soluble in hot water, and are prepared from the potassium salt by double decomposition. The *barium* and *lead salts* crystallise in flat needles containing 5 mol. water; the *calcium salt* in small tables containing 4 mol. water; the *silver salt* in shining needles.

The potassium salt of γ benzoyl-sulphothymolic acid is very much like the α salt, but contains 3 mol. water.

TIN. Blocks of Banka tin exposed to the open air at St. Petersburg in the cold winter of 1867–1868 acquired a crystalline structure and partly crumbled to a granulo-crystalline powder. The internal cavities became lined with a metallically lustrous film, while the crystalline structures themselves appeared dull (Fritzsche, *Phil. Mag.* [4] xxxviii. 207).

Calvert a Johnson (*Chem. Soc. J.* [2] iv. 435) have examined the action of sulphuric acid of different strengths upon tin, with the following results. By two hours' action of 50 c. c. acid on 1 c. c. metal, the following quantities were dissolved:

	Grams.		Grams.
By $H^{2}SO^{4}$ at 150° .	3·010	By $H^{2}SO^{4}.3H^{2}O$ at 130°	0·215
„ $H^{2}SO^{4}.H^{2}O$ at 150°	0·640	„ $H^{2}SO^{4}.4H^{2}O$ „	0·140
„ $H^{2}SO^{4}.2H^{2}O$ at 150°	0·470		

The action of pure hydrogen sulphate, $H^{2}SO^{4}$, is attended with evolution of sulphurous oxide and separation of sulphur; with $H^{2}SO^{4}.H^{2}O$ sulphurous oxide is likewise evolved: with $H^{2}SO^{4}.2H^{2}O$ hydrogen sulphide goes off, together with the sulphurous oxide; and with the two weaker hydrates hydrogen sulphide is the chief gaseous product.

Alloys. Riche (*Compt. rend.* lxvii. 1138) has examined the physical properties of alloys of tin and copper in various proportions from $Sn^{5}Cu$ to $SnCu^{15}$ (gun-metal). With regard to density, it appears that the contraction increases pretty regularly from the alloys richest in tin to the alloy $SnCu^{2}$, but that it then increases very rapidly, attaining its maximum in the alloy $SnCu^{3}$. The density then diminishes down to the alloy $SnCu^{5}$, beyond which it again regularly increases, but only so far that the density of the alloy richest in copper still remains less than that of the alloy $SnCu^{3}$. This alloy differs in its properties from all the rest, being so brittle that it may be pulverised in a mortar, and forming bluish crystalline grains not resembling either tin or copper. The solidifying point of the alloys $SnCu^{3}$ and $SnCu^{4}$ is intermediate between the melting point of antimony and the boiling point of cadmium.

Chlorides. 1. *Stannous Chloride*, $SnCl^{2}$ (Gerlach, *Dingl. pol. J.* clxxxvi. 131; *Bull. Soc. Chim.* [2] ix. 248; *Jahresb.* 1867, 272).—Well-defined crystals of this salt, as well as the needle-shaped crystals often found in commerce, and the lamino-scaly crystals which separate from solutions containing a considerable proportion of stannic oxide, all have the composition $SnCl^{2}.2H^{2}O$. Stannous chloride likewise crystallises with the same amount of water from a solution containing equivalent quantities of stannous and stannic chlorides (contrary to former statements, v. 807). The specific gravities of aqueous solutions of stannous chloride are given in the following table, in which *p* denotes the percentage of crystallised salt, $SnCl^{2}.2H^{2}O$, and *d* the specific gravity at 15°:

p	*d*	*p*	*d*	*p*	*d*
0	1·0000	30	1·2300	60	1·5823
5	1·0331	35	1·2779	65	1·6598
10	1·0684	40	1·3298	70	1·7452
15	1·1050	45	1·3850	75	1·8399
20	1·1442	50	1·4451		
25	1·1855	55	1·5106		

On the reaction of stannous chloride with arsenious and arsenic acid, see ARSENIC (pp. 220, 222); on its reaction with metallic solutions and sulphurous acid (p. 1065).

Stannic Chloride, $SnCl^4$ (Gerlach, *Dingl. pol. J.* clxxviii. 49; *Bull. Soc. Chim.* [2] iv. 483; *Jahresb.* 1865, p. 237).—The specific gravity of the anhydrous chloride is 2·234 at 15°. When it is rapidly mixed with water, the liquid becomes heated to the boiling point; on gradual addition of water, a point is reached at which the hot aqueous solution is denser than the undissolved aqueous chloride. The dissolution is accompanied by a diminution of volume greater than that hitherto observed in any other mixture. In the following table, P denotes the percentage of anhydrous chloride in the solution; D the specific gravity of the solution at 15°; V the volume of 100 pts. by weight, that of 100 parts by weight of water being = 100; V′ the volume which 100 parts by weight would occupy if no contraction took place; V″ the volume of the mixture, that of the sum of the constituents being = 100.

P	D	V	V′	V″
0	1·000	100·00	100·00	100·00
10	1·082	92·42	94·48	97·82
20	1·174	85·18	88·95	95·76
30	1·279	78·19	83·43	93·72
40	1·404	71·22	77·90	91·42
50	1·556	64·26	72·38	88·78
60	1·743	57·37	66·86	85·81
70	1·973	50·68	61·33	82·63
80	—	—	55·81	—
90	—	—	50·28	—
100	2·234	44·76	44·76	100·00

Gerlach has obtained the hydrates $SnCl^4.3H^2O$, $SnCl^4.5H^2O$, and $SnCl^4.8H^2O$ in the crystalline form. When 1 mol. stannic chloride (259·48 pts.) is mixed with 1 mol. water (18 pts.), two thirds of the stannic chloride remain unaltered, whilst the remaining third forms the hydrate $SnCl^4.3H^2O$, which sinks in the excess of stannic chloride. When 1 mol. stannic chloride is mixed with 2 mol. water, the whole solidifies while still hot to a solid mass enclosing ⅓ of the chloride in the anhydrous state. 1 mol. stannic chloride dissolves in 3 mol. water with great evolution of heat, the temperature rising to the boiling point, and forms a clear liquid which deposits the hydrate $SnCl^4.3H^2O$ at 60°, and solidifies to a mass when quite cold. The fumes which stannic chloride emits in moist air, and the efflorescences which form on the edges of vessels containing it, likewise consist of the trihydrated salt. A mixture of stannic chloride with 4 mol. water yields transparent pointed crystals having the composition $SnCl^4.4H^2O$; these however are regarded by Gerlach as consisting of the trihydrate with enclosed solidified mother-liquor. The pentahydrate, $SnCl^4.5H^2O$, separates gradually from duly concentrated solutions in white, turbid, very deliquescent monoclinic crystals which melt at a gentle heat. Less concentrated solutions yield at very low temperatures large transparent crystals of the octohydrate, $SnCl^4.8H^2O$,* still more deliquescent than the pentahydrate. This latter is regarded by Gerlach as the best adapted for industrial use. The following table (p. 1094) exhibits the specific gravities (D) of aqueous solutions containing the percentages (P) of crystallised pentahydrated stannic chloride, for the temperature of 15°.

The aqueous solution of stannic chloride acts as an acid towards most metallic oxides; it takes up 1 mol. stannic hydrate, forming a soluble oxychloride, and reacts in a similar manner with other oxides soluble in hydrochloric acid. Recently prepared solutions of stannic chloride are not coloured by stannous chloride, but those which have been kept for some time acquire thereby a yellow colour, arising, according to Gerlach, from the formation of stannic oxychloride. In a concentrated limpid solu-ion of stannic oxychloride, stannous chloride dissolves with dark brown colour Gerlach).

A solution containing the chlorides of sodium, potassium, lithium, cæsium, and ubidium, together with free hydrochloric, gives with stannic chloride a crystalline recipitate consisting of nearly pure *cæsium stannochloride*, $Cs^2Sn^{iv}Cl^6$ or $2CsCl.SnCl^4$ Sharples, *Sill. Am. J.* [2] xlvii. 178; *Zeitschr. f. Chem.* [2] v. 406).

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* Nöllner (*Zeitschr. f. Chem.* [2] i. 445) obtained from a solution of stannic chloride prepared by eating stannous chloride with nitromuriatic acid and exposed to a winter temperature, transparent olourless rhombic octahedrons of the salt $SnCl^4.9H^2O$, which deliquesced when heated above 19°.

Density of Aqueous Solutions of $SnCl^4.5H^2O$ at 15°.

P	D	P	D	P	D	P	D
0	1·000	25	1·1581	50	1·3661	75	1·6543
1	1·006	26	1·165	51	1·376	76	1·669
2	1·012	27	1·173	52	1·386	77	1·683
3	1·018	28	1·180	53	1·396	78	1·698
4	1·024	29	1·187	54	1·406	79	1·712
5	1·0298	30	1·1947	55	1·4154	80	1·7271
6	1·036	31	1·202	56	1·426	81	1·743
7	1·042	32	1·210	57	1·437	82	1·759
8	1·048	33	1·218	58	1·447	83	1·775
9	1·053	34	1·226	59	1·458	84	1·791
10	1·0593	35	1·2338	60	1·4684	85	1·8067
11	1·066	36	1·242	61	1·480	86	1·824
12	1·072	37	1·250	62	1·491	87	1·842
13	1·078	38	1·259	63	1·503	88	1·859
14	1·084	39	1·267	64	1·514	89	1·876
15	1·0905	40	1·2755	65	1·5255	90	1·8939
16	1·097	41	1·284	66	1·538	91	1·913
17	1·104	42	1·293	67	1·550	92	1·932
18	1·110	43	1·302	68	1·563	93	1·950
19	1·117	44	1·310	69	1·575	94	1·969
20	1·1236	45	1·3193	70	1·5873	95	1·9881
21	1·130	46	1·329	71	1·601		
22	1·137	47	1·338	72	1·614		
23	1·144	48	1·347	73	1·627		
24	1·151	49	1·357	74	1·641		

Stannic chloride added to *amyl alcohol* cooled by a freezing mixture, unites with it, producing the compound $SnCl^4.2C^5H^{12}O$, which forms colourless tabular deliquescent crystals, instantly resolved by water into stannous chloride, hydrochloric acid, and amyl alcohol. The crystals heated to 100° are decomposed, chiefly in the manner represented by the equation: $2(SnCl^4.2C^5H^{12}O) = SnCl^4.3H^2O + SnCl^2.H^2O + 3C^5H^{10} + C^5H^{10}Cl^2$ (Bauer a. Klein, *Zeitschr. f. Chem.* [2] iv. 370).

Iodide. Crystallised stannic iodide is most easily obtained by gradually adding 4 pts. of iodine in small portions to 1 pt. of tin-foil immersed in 6 pts. carbon bisulphide contained in a closed vessel and well cooled, decanting the solution as soon as it acquires a pure yellow colour, and leaving it to evaporate; 1 pt. carbon bisulphide dissolves at ordinary temperatures 1·45 pt. stannic iodide (R. Schneider, *Jahresb.* 1866, p. 229).

Stannic Oxide, Acids, and Salts. The distinguishing characteristics of stannic and metastannic acids have been further examined by Barfoed (*J. pr. Chem.* ci. 365; *Jahresb.* 1867, p. 267). *Reaction with Caustic Soda.*—Ordinary or *a*-stannic acid dissolves easily in soda-ley, and is not precipitated by the excess of the alkali. Meta- or *b*-stannic acid is completely precipitated by soda-ley from a moderately dilute acid solution, in the form of sodium metastannate.* The precipitate is easily soluble in water, insoluble in dilute soda-ley and in weak spirit. When dried it forms white, gummy granules, and when pulverised is easily dissolved by treatment with hydrochloric acid and subsequent addition of water. Sodium metastannate precipitated by soda-ley from the hydrochloric solution of metastannic acid, washed with alcohol and dried at 100°, was found to have the composition $Na^2O.9SnO^2 + 8H^2O$.

Reaction with Hydrochloric Acid.—The hydrochloride of *a*-stannic acid dissolves easily in hydrochloric acid of sp. gr. 1·1. When this solution, which alters but slowly, is distilled, the whole of the tin passes over as tetrachloride. The hydrochloride of metastannic acid is insoluble in hydrochloric acid of sp. gr. 1·1, and is easily purified by washing with such acid. The recently prepared perfectly pure compound forms a colourless solution; the yellow colour which it commonly exhibits arises partly from residual nitric acid (which sets chlorine free), partly from iron and other impurities. The solution decomposes rather quickly, and with greater facility as it is more dilute and contains less acid; the solid compound likewise undergoes a similar decomposition and becomes insoluble. By strong hydrochloric acid, recently prepared and still moist metastannic acid is gradually converted into stannic acid; after drying at 100° it undergoes the same change, but less easily.* The proportion of metastannic acid thus converted increases with the quantity of hydrochloric acid, the time of contact, and the temperature. Consequently the hydrochloric acid solution of metastannic acid always contains more or less stannic acid, which may be separated in the manner above mentioned; and herein may be found an explanation of the fact that the hydrochloric acid solution of metastannic acid likewise yields by distillation a certain quantity of stannic chloride.

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* According to Frémy, sodium metastannate dissolves slowly, but completely, in water (v. 821).

Reaction with Hydrogen Sulphide.—The precipitates formed by hydrogen sulphide in both modifications of stannic acid are always mixtures of stannic sulphide with *a* or *b* stannic hydrate: they are not, however, identical. Recently prepared, concentrated and acid solutions of stannic chloride form a light yellow precipitate which retains its colour unaltered; non-acid solutions yield a reddish-yellow, and very dilute solutions a white precipitate, which turns yellow only when washed. All these precipitates in the moist state, after washing, contain, besides stannic sulphide, variable quantities of *a*-stannic acid; they dissolve easily in alkaline leys and in warm dilute hydrochloric acid, the solution exhibiting all the reactions of *a*-stannic acid. During drying they continually give off hydrogen sulphide, assume a dark brown or nearly black colour, and are then no longer perfectly soluble in soda-ley. Metastannic acid is very slowly attacked by hydrogen sulphide. Dilute hydrochloric acid solutions of it form, with hydrogen sulphide, a white precipitate consisting essentially of metastannic hydrate; concentrated solutions, a yellow-brown precipitate; both precipitates, when kept for 24 hours in closed vessels, assume a dark brown colour, and when dried turn black and give off hydrogen sulphide. Since, when metastannic acid is dissolved in strong hydrochloric acid, a certain portion, variable according to circumstances, is converted into stannic acid, it follows that these precipitates are mixtures of those which would be produced from pure stannic and pure metastannic acid; they therefore contain stannic and metastannic acid together with stannic sulphide, and are on the average less rich in sulphur than those which are formed from stannic acid. When treated with soda-ley, they leave a white residue of sodium metastannate, and likewise yield with colourless ammonium sulphydrate a white precipitate, which disappears on heating the liquid. In warm potash, ammonia, and hydrochloric acid they dissolve with moderate facility with aid of heat.

From the preceding reactions, Barfoed regards treatment with soda-ley as the best means both for the qualitative detection and for the separation of the two stannic acids. For quantitative estimation he determines the total quantity of tin in one aliquot part of the solution, and the amount of metastannic acid in another by precipitation with soda-ley. In the filtrate and wash-water thereby obtained, the *a*-stannic acid may, for verification, be separated by hydrogen sulphide from the solution acidulated with hydrochloric acid, and estimated by known methods.

Musculus (*Compt. rend.* lxv. 961) describes certain hydrates intermediate between ordinary stannic hydrate, ($SnO^2.H^2O$), and metastannic hydrate, ($Sn^5O^{10}.5H^2O$), and produced from the former by keeping under water. Recently prepared stannic hydrate (precipitated from stannic chloride by ammonia) dissolves easily in strong nitric and hydrochloric acid, also in caustic potash, and is precipitated by a large excess of potash as a crystalline powder. After several hours' immersion in water, it loses its solubility in nitric acid, and when treated in potassic solution with excess of potash, yields an amorphous precipitate (second hydrate). After several days it becomes insoluble in hydrochloric acid, but still remains soluble in potash (third hydrate).

From metastannic acid, into which these two hydrates are ultimately converted, hey are distinguished by the fact that they still dissolve in strong hydrochloric and itric acids in presence of alkaline chlorides. Metastannic acid, treated with boiling oncentrated potash-ley, yields at first the potassium salts corresponding to the third nd second hydrate, which separate in consequence of their sparing solubility; it is nly when the solution has become very concentrated that crystals of ordinary potas-ium stannate are formed. The potassium salt of the second hydrate contains 2 at. in to 1 at. potassium; that of the third hydrate 3 at. tin to 1 at. potassium; the orresponding acids are therefore represented by the formulæ:

$Sn^2H^4O^6$ for the second hydrate,
$Sn^3H^6O^9$ for the third hydrate.

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* On the conversion of stannic into metastannic acid, see v. 820.

When metastannic hydrate is boiled with concentrated hydrochloric acid, and the liquid separated from the precipitate is saturated with hydrochloric acid gas, a precipitate is formed containing the hydrate $Sn^3H^6O^9$; the remaining acid solution leaves on evaporation a crystalline, very deliquescent acid, partly soluble in ether, and consisting, according to Musculus, of a mixture of crystallised hydrated stannic chloride, and the hydrochloride of the hydrate $Sn^2H^4O^6$. From these observations Musculus infers the existence of a series of polystannic acids analogous to the polysilicic acids.

Sodium Stannate. $Na^2Sn^2O^3$ or $Na^2O.SnO^2$.—Of this salt three hydrates have been previously obtained, containing 3, 8, and 9 mol. water (v. 819). Another hydrate, $Na^2SnO^3 + 10H^2O$, crystallises in large prisms from dilute solution by evaporation at a low temperature. These crystals form only in pure solutions, especially in such as are free from excess of soda; they are very efflorescent, and decompose in aqueous solution at 80°, with separation of stannic hydrate; addition of soda prevents this decomposition (Scheurer-Kestner, *Bull. Soc. Chim.* [2] viii. 389).

Respecting stannates containing platinum, see p. 1077.

Selenides (Schneider, *Pogg. Ann.* cxxvii. 624; *Bull. Soc. Chim.* [2] vi. 449; *Jahresb.* 1866, p. 227).—The ***monoselenide*** or ***stannous selenide***, SnSe, may be obtained crystallised and quite pure, by heating finely pulverised selenium with fused anhydrous stannous chloride till the mixture appears transparent in thin layers: $2SnCl^2 + Se = SnSe + SnCl^4$. Stannic chloride then volatilises, and the stannous selenide, which remains dissolved in the excess of stannous chloride, crystallises out on cooling. The product which Uelmann obtained (v. 821) by fusing 3 pts. tin with 2 pts. selenium generally contains free tin; it may be converted into the pure monoselenide by fusion with stannous chloride as above.

Stannous selenide crystallises in prisms or laminæ resembling stannous sulphide, and probably isomorphous with it; the crystals have a sp. gr. of 5·24, a steel-grey colour and metallic lustre; may be heated in a close vessel or in a stream of hydrogen without alteration, but are slowly converted into stannic oxide when heated in the air, and are scarcely attacked by aqueous soda or ammonia, even at the boiling heat (in which respect they differ from the monoselenide prepared in the wet way), but are dissolved with red colour by the sulphides and selenides of the alkali-metals. Boiling hydrochloric acid dissolves them slowly, with solution of hydrogen selenide: strong nitric acid at the boiling heat colours them brown-red from separation of selenium, and ultimately converts them into selenious and selenic acid; nitromuriatic acid dissolves them with facility.

An intimate mixture of 2 mol. stannous selenide (4 pts.) and 2 mol. iodine (5 pts.) liquefies at a gentle heat, and solidifies to a red-brown mass, which is dissolved by carbon bisulphide to a yellowish liquid, with a residue of stannic selenide (with small quantities of stannous selenide and free selenium). The solution when left to evaporate first yields dark red crystals of selenium; then, to the last drops, chrome-red octahedral crystals of stannic iodide: $2SnSe + I^4 = SnI^4 = SnSe^2$. With twice the quantity of iodine the reaction takes place with equal facility, and without separation of iodine: $SnSe + I^4 = SnI^4 + Se$; on treating the product with carbon bisulphide, the greater part of the selenium remains undissolved. A solution of iodine in carbon bisulphide acts on stannous selenide in the same way at ordinary temperatures, the excess of iodine remaining in solution uncombined, together with selenium; compounds of selenium and iodine cannot thérefore be obtained in this manner. *Bromine* acts on stannous selenide in a similar manner to iodine, combining with it in the cold with a hissing noise and rise of temperature; more quietly when added with agitation to the selenide immersed in carbon bisulphide. The products are stannic bromide and stannic selenide, or stannic bromide and selenium, according to the proportions used: $2SnSe + 2Br^2 = SnBr^4 + SnSe^2$; and $SnSe + 2Br^2 = SnBr^4 + Se$. When more than 2 mol. bromine are used to 1 mol. stannous selenide, selenium bromides are likewise formed.

The ***biselenide*** or ***stannic selenide***, $SnSe^2$, is very easily decomposed by heat, and cannot therefore be prepared either by heating a mixture of its elements, or by a process similar to that generally used for preparing the bisulphide (mosaic gold); the compound described by Little (v. 882) as biselenide of tin was probably only monoselenide. The biselenide may however be prepared by means of the above-mentioned reaction between iodine and the monoselenide. 5 pts. of iodine are triturated to a homogeneous mixture with 8 to 10 pts. of crystallised stannic iodide; this is intimately mixed by gentle trituration with 4 pts. of levigated stannous selenide, and carbon bisulphide is added, with rapid stirring, in sufficient quantity to form a pasty mass, which is then treated with a large quantity of carbon bisulphide to dissolve the stannic iodide. After washing with carbon bisulphide, the stannic selenide remains as an indistinctly crystalline powder, which when dried has a specific gravity of 4·85, and a dark red-brown colour, becoming darker at 100°. It is not attacked by water or dilute acids, scarcely by strong boiling hydrochloric acid; reacts like the monoselenide with nitric and nitromuriatic acid. Heated with strong sulphuric acid, it forms an olive-green solution, from which, when poured into a large quantity of water, selenium is separated as a red powder, while stannic sulphate remains in solution. In caustic fixed alkalis and ammonia the biselenide dissolves at ordinary temperatures, forming blood-red solutions, from which it is precipitated by acids. 1 mol. stannic selenide gently heated with 2 mol. iodine melts to a dark red liquid, which, when further heated, yields a sublimate of iodine and afterwards of stannic iodide, and after solidification may be resolved by carbon bisulphide into soluble stannic iodide and a residue of selenium: $SnSe^2 + 2I^2 = SnI^4 + Se$. A solution of iodine in carbon bisulphide acts on stannic selenide in the same manner. Bromine also produces a similar reaction.

Sulphides. The statement of Proust (v. 823) that stannic sulphide and chloride are formed by the action of sulphur on fused stannous chloride does not appear to be correct. The reaction is in fact analogous to that which takes place with selenium (p. 1096), the products being stannic chloride, which volatilises, and stannous sulphide, which remains dissolved in the excess of stannous chloride, and separates in crystals on cooling (Schneider).

Platinum-tin Compounds (Schneider, *Pogg. Ann.* cxxxvi. 105; *Zeitschr. f. Chem.* [2] v. 613).—When a solution of platinic chloride containing 0·01 grm. platinum in a cubic centimetre is mixed with a moderately strong solution of stannous chloride in hydrochloric acid, the mixture, if kept in a closed vessel, gradually turns dark brown, and yields a brown precipitate with ammonia. To precipitate all the platinum requires at least 3 mol. stannous chloride to 1 mol. platinic chloride. The reaction may perhaps be supposed to take place as represented by the equation:

$$2PtO^2 + 6SnO = Pt^2O + 3Sn^2O^3,$$

assuming the formation of a hypoplatinous oxide containing only half as much oxygen as platinous oxide. The compound $Pt^2O.3SnO^2$ or $Pt^2O.3SnO.3SnO^2$ may accordingly be designated as *hypoplatinoso-stannous stannate* (Schneider calls it *zinnsaures Platinoxydul-zinnoxydul*). The brown compound treated with soda-ley does not, however, yield the supposed oxide of platinum, but a black substance, $Na^2Pt^2Sn^2O^6$ or $Pt^2O.Na^2O.2SnO^2$, which may be called *sodio-hypoplatinous stannate*. Hypoplatinoso-stannous stannate, fused with potassium carbonate and sulphur, yields potassio-platinous sulphostannate, $K^2\overset{''}{Pt}{}^2Sn^{iv}S^6$ (p. 1077). The salt thus obtained was formerly supposed by Schneider to contain oxygen as well as sulphur; but more recent experiments have shown that this supposition is incorrect.

TITANIUM. *Titano-phosphoric chloride*, $TiPCl^9 = TiCl^4.PCl^5$, analogous to the tin compound, $SnCl^4.PCl^5$, described by Casselmann (v. 809), is produced, according to Tüttschew (*Ann. Ch. Pharm.* cxli. 111), by heating an intimate mixture of 1 pt. titanic oxide, TiO^2 (15 grm.) and 3 mol. phosphorus pentachloride (115 grm.) in a retort, continuing the heat for a considerable time after the reaction is completed, in order to volatilise the phosphorus oxychloride which is likewise formed: $TiO^2 + 3PCl^5 = TiCl^4.PCl^5 + 2POCl^3$. It is also formed, according to Weber (*Pogg. Ann.* cxxxii. 452), by the direct mixture of the component chlorides, or by passing their vapours together through a red-hot glass tube; but the product thus obtained is contaminated with portions of the uncombined chlorides. It may be obtained pure by passing chlorine into a mixture of phosphorus trichloride with excess of titanic chloride, and heating the product gently towards the end in a stream of chlorine.

Titanophosphoric chloride is a lemon-yellow, indistinctly crystalline mass, which dissolves without decomposition in ether, and remains as a gummy mass on evaporating the solution; it is also dissolved in small quantity by phosphorus oxychloride, but cannot easily be separated from the solution. Water and moist air decompose it rapidly. Placed under a receiver with water and quick lime, it leaves, after a few days, titanic hydrate which is quite free from phosphoric acid, and, after remaining for some time, contains only a trace of chlorine (Tüttschew). According to Weber, it volatilises when heated, without previous fusion, and condenses to a yellow powder n cooling. It is very hygroscopic, and dissolves in dilute acids to a yellow liquid, which after some time deposits a gelatinous precipitate.

The compound $TiCl^4.POCl^3$ is formed by dropping phosphorus oxychloride into excess of titanic chloride, and is obtained pure by warming the solidified mixture till it melts completely, and decanting the portion which remains liquid after cooling, from the crystalline mass which constitutes the compound in question. It is colourless, easily fusible, and very hygroscopic (Weber).

A mixture of titanic chloride and sulphur chloride, saturated with chlorine gas and gently warmed in a stream of chlorine, yields *titano-sulphurous chloride*, $2TiCl^4.SCl^4$, as a sulphur-yellow powder, which is decomposed at a stronger heat, is very deliquescent, and dissolves in dilute nitric acid, with formation of sulphuric, hydrochloric, and titanic acids. The compound which H. Rose obtained (v. 536) appears to have been merely a mixture (Weber).

Titanic Hydrates (Tüttschew, *loc. cit.*).—The hydrate obtained by the action of moist air on titanophosphoric chloride has, after drying over oil of vitriol, the composition of the normal hydrate, or titanic acid, TiH^4O^4. At 110°–120° it gives off 15·50 p. c. water, and is converted into the first anhydride, TiH^2O^3. In appearance and properties the normal hydrate resembles the hydrate obtained by boiling with sulphuric acid, which after drying over oil of vitriol has the same composition. The latter (*b*-titanic acid, metatitanic acid, or metatitanic hydrate) heated to 120°, leaves the hydrate $Ti^3H^8O^{10}$, and at 140° the hydrate $Ti^3H^4O^8$, previously observed by Demoly. The hydrate obtained by precipitation with ammonia, to which Demoly assigned the formula $3TiO^2.5H^2O$ or $Ti^3H^{10}O^{11}$, was found by Tüttschew, after drying in a vacuum, to contain $Ti^3H^6O^9$. At 140° this hydrate is converted into $Ti^2H^2O^5$. From these results Tüttschew infers the existence of a series of polytitanic acids analogous to the polysilicic acids, and formed from normal titanic acid according to the general equation:

$$nTiH^4O^4 - mH^2O = Ti^nH^{4n-2m}O^{4n-m}.$$

The following table exhibits the composition of the hydrates of titanic acid as determined by the observations of different chemists, by no means always accordant:

a Titanic acid (precipitated by ammonia).

Air-dried	$TiO^2.3H^2O = TiH^6O^5$	Merz.[*]
"	$TiO^2.2H^2O = TiH^4O^4$	
"	$3TiO^2.5H^2O = Ti^3H^{10}O^{11}$	Demoly.[†]
Dried in a vacuum	$TiO^2. H^2O = Ti^3H^6O^9$	Tüttschew.
" over sulphuric acid	$TiO^2. H^2O = TiH^2O^3$	Merz.
" at 60°	$4TiO^2.3H^2O = Ti^4H^6O^{11}$	Merz.
" " 100°	$2TiO^2. H^2O = Ti^2H^2O^5$	Demoly, Merz.
" " 140°	$2TiO^2. H^2O = Ti^2H^2O^5$	Tüttschew.
" over sulphuric acid in a vacuum	$2TiO^2. H^2O = Ti^2H^2O^5$	Rose.[‡]
" at 140°, or in a vacuum	$3TiO^2.2H^2O = Ti^3H^4O^8$	Demoly.

b or Metatitanic acid (precipitated by boiling the sulphuric acid solution).

Dried over sulphuric acid	$TiO^2.2H^2O = TiH^4O^4$	Tüttschew.
" at 120°	$3TiO^2.4H^2O = Ti^3H^8O^{10}$	Tüttschew.
Air-dried	$TiO^2. H^2O = TiH^2O^3$	Merz.
Dried over sulphuric acid, or at 60°	$2TiO^2. H^2O = Ti^2H^2O^5$	Merz.
" at 140°	$3TiO^2.2H^2O = Ti^3H^4O^8$	Demoly, Tüttschew.
" at 100°	$3TiO^2. H^2O = Ti^3H^2O^7$	Merz.

Hydrate formed by moist air from Titanophosphoric chloride.

Dried over sulphuric acid	$TiO^2.2H^2O = TiH^4O^4$	Tüttschew.
" at 110°–120°	$TiO^2. H^2O = TiH^2O^3$	Tüttschew.

For the preparation of pure titanic acid, and its separation from zirconia and ferric oxide, the following method is given by Streit a. Franz (*J. pr. Chem.* cviii. 65; *Zeitschr. f. Chem.* [2] vi. 256). Finely pulverised and levigated rutile is intimately mixed with three times its weight of potassium carbonate, and fused in a Hessian crucible, and the fused mass is poured in a thin layer upon an iron plate. It is then finely pulverised and exhausted with cold water, whereby silicate and tungstate of potassium are removed, while potassium titanate and ferric oxide remain undissolved. The residue is dissolved in crude hydrochloric acid, rise of temperature being prevented as far as possible; the resulting solution is generally somewhat clouded

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[*] *Jahresb.* 1866, p. 197.

[†] *Ibid.* 1849, p. 270.

[‡] *Ann. Ch. Pharm.* lii. 268.

SILICIC SULPHYDRATE (chlorinated). $\left.\begin{matrix}SiCl^3\\H\end{matrix}\right\}S$. *Silicic Mercaptan.*—This compound, analogous to methyl-mercaptan, $\left.\begin{matrix}CH^3\\H\end{matrix}\right\}S$, is produced by passing a mixture of hydrogen sulphide and vapour of silicic chloride through a red-hot tube:

$$SiCl^4 + H^2S = HCl + SiCl^3HS.$$

It is a colourless liquid, boiling at 196°, smelling of hydrogen sulphide and silicic chloride, and decomposed by moist air, with formation of silica, hydrochloric acid, and sulphur. With absolute alcohol it forms normal silicic ether, $Si(OC^2H^5)^4$, the compound $Si(OC^2H^5)^3HS$ being apparently also formed as an intermediate product. Dry bromine decomposes silicic mercaptan, with rapid evolution of hydrobromic acid and formation of silicic chlorobromide, $SiCl^3Br$:

$$2SiCl^3HS + 3Br^2 = 2SiCl^3Br + Br^2S^2 + 2HBr.$$

The chlorobromide, separated by distillation from the bromine sulphide, is a colourless liquid, which fumes in the air, boils at 80°, and has a vapour-density = 7·25 (calc. 7·42). With water it is resolved into silica, hydrochloric acid, and hydrobromic acid. Silicic chlorobromide is likewise obtained by heating silicic chloroform to 100° for some time with bromine, and submitting the product to fractional distillation (Friedel a. Ladenburg, *Bull. Soc. Chim.* [2] vii. 472).

SILICOFLUORIDES. The specific gravity of potassium silicofluoride is 2·6649–2·6655 at 17·5°; of the sodium salt, 2·7547 at 17·5°; of the barium salt, 4·2741 at 21°, all referred to an equal volume of water at 15° as unity (Stolba, *J. pr. Chem.* xcvii. 503).

Potassium Silicofluoride, recently precipitated in the cold, collected on a filter, and left to itself for 24 hours, retains from 63 to 65 p. c. water; when precipitated from a hot solution, it retains 45 to 46 p. c. The gelatinous precipitate appears crystalline under the microscope, especially if moistened with a little alcohol. It is less soluble in saline solutions than in pure water: 1 pt. of the salt requires for solution 833 pts. water at 17·5°; 24,066 pts. of a solution of potassium sulphate (of 9·92 p. c.) at 17°; 125,000 of an 18·4 p. c. solution of potassium nitrate at 15°; 1735 pts. of an 8·8 p. c. solution of the same salt at 100°. Aqueous sal-ammoniac of 26·3 p. c. dissolves it more easily than a 5 p. c. solution of the same salt. Acids dissolve potassium silicofluoride more easily than water, but decompose it at the same time, usually with emission of vapours of silicon fluoride. In hydrochloric acid, however, the salt dissolves without formation of visible decomposition-products, and more abundantly in proportion as the acid is stronger. When potassium silicofluoride is ignited with 1 to 2 pts. of sal-ammoniac, ammonium silicofluoride is given off, and potassium chloride remains behind. When the potassium salt is boiled with carbonate of magnesium or calcium, in presence of water, fluoride of magnesium or calcium is formed, but the decomposition is never complete (Stolba, *J. pr. Chem.* ciii. 396; *Zeitschr. f. Chem.* [2] iv. 576).

Caesium Silicofluoride, $2CsF.SiF^4$, is prepared by precipitating cæsium chloride with cupric silicofluoride, and washing the precipitate on a filter till all the copper salts are removed; it forms anhydrous crystals. When precipitated by alcohol it is not distinctly crystalline, but from a hot solution it separates in shining octohedrons truncated by cubic faces. By spontaneous evaporation, cubes with truncated summits are obtained. Sp. gr. 8·3756 at 17°. One part of the salt dissolves in 166 pts. water at 17°, and in a much smaller quantity of hot water, but it is insoluble in alcohol. Ignited with sal-ammoniac it leaves pure cæsium chloride. It is easily and completely decomposed by lime-water (Stolba, *J. pr. Chem.* ciii. 410).

Rubidium Silicofluoride, $2RbF.SiF^4$, is precipitated from hot solutions as a distinctly crystalline powder, appearing under the microscope to consist of transparent cubes modified with octohedral and dodecahedral faces; the precipitate formed in the cold is less crystalline. Sp. gr. 3·3383 at 20° referred to water at the same temperature. 1 pt. of the salt dissolves in 614 pts. water at 20°, in 73·8 pts. at the boiling heat. The aqueous solution has an acid taste and reaction; a solution saturated at 20° has a sp. gr. of 1·0013. The salt is more soluble in acids than in water; insoluble in alcohol; reacts with alkalis like the potassium and sodium salts (Stolba, *J. pr. Chem.* cii. 1).

Cupric Silicofluoride, $CuF^2.SiF^4$, may be prepared by dissolving cupric carbonate in dilute silicofluoric acid, or by boiling barium silicofluoride with the solution of an equivalent quantity of cupric sulphate (adding a small quantity of the barium salt towards the end of the process till the sulphuric reaction disappears), and evaporating in a vacuum at 10° to 22°. It forms crystals belonging to the hexagonal paraphthalic acid. Hence it appears that ordinary toluic acid, which melts at 176°, is paratoluic acid. Orthoxylene, obtained by distilling paraxylic acid with lime (p. 293), treated with dilute nitric acid, is slowly oxidised to toluic acid, which is slightly soluble in cold water, moderately soluble in boiling water, and crystallises from a dilute solution in splendid, long, transparent, spicular crystals melting at 102°; this is orthotoluic acid; its calcium salt, $(C^8H^7O^2)^2Ca + 2H^2O$, and barium salt, $(C^8H^7O^2)^2Ba$, are very soluble in water, and crystallise in slender needles (Bieber a. Fittig, *Zeitschr. f. Chem.* [2] vi. 496). Lastly, by oxidising monobromoxylene (from coal-tar xylene) with chromic acid, two bromotoluic acids, $C^8H^7BrO^2$, are obtained, which form calcium salts of different solubility, the less soluble crystallising in needles containing $(C^8H^6BrO^2)^2Ca + 3H^2O$, the more soluble in smaller needles containing $8H^2O$. The acid separated from the former of these salts melts at 205°–206°, that from the latter at 185°–189°; and by agitating the brominated acid melting at 205°–206° with sodium-amalgam for two days, the sodium salt of a toluic acid is obtained which, when separated by hydrochloric acid, forms slender needles melting at 90°–93°, or about 10 degrees lower than orthotoluic acid. This toluic acid, oxidised with chromic acid, yields isophthalic or metaphthalic acid, and consequently consists of metatoluic acid.

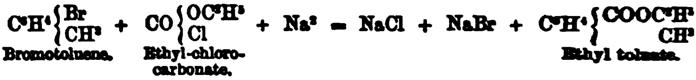
Paratoluic or ordinary toluic acid is also produced: *a.* By distilling potassium sulphotoluate with potassium cyanide, whereby tolyl cyanide is obtained, and saponifying this compound with alcoholic potash:

$$C^6H^4(CH^3).SO^3K + CNK = SO^3K^2 + C^6H^4(CH^3).CN$$

and

$$C^6H^4(CH^3).CN + 2H^2O = NH^3 + C^6H^4(CH^3).CO^2H.$$

The acid thus obtained melts at 175°–176° (Merz, *Zeitschr. f. Chem.* [2] iv. 331–*β*. Together with one of the other modifications, by heating monobromotoluene (b. p. 178°–185°) with ethyl chlorocarbonate and sodium-amalgam in a flask fitted with an upright condenser and placed in a sand-bath:



$$\underset{\text{Bromotoluene.}}{C^6H^4\left\{\begin{matrix}Br\\CH^3\end{matrix}\right.} + \underset{\text{Ethyl-chloro-carbonate.}}{CO\left\{\begin{matrix}OC^2H^5\\Cl\end{matrix}\right.} + Na^2 = NaCl + NaBr + \underset{\text{Ethyl toluate.}}{C^6H^4\left\{\begin{matrix}COOC^2H^5\\CH^3\end{matrix}\right.}$$

On exhausting the product with ether, distilling off the portion which boils below 180°, decomposing the residue with alcoholic potash, precipitating with hydrochloric acid, recrystallising from water, and distilling, toluic acid is obtained contaminated with a more fusible acid, the whole melting at 153°; and by repeatedly treating it with a quantity of boiling water less than sufficient for complete solution, the toluic acid is at length obtained pure and melting at 176° (Wurtz, *Compt. rend.* lxvii. 1298).

Bromotoluic Acids.—*Metabromotoluic acid*, $C^8H^7BrO^2$, produced by oxidising monobromoxylene (from coal-tar xylene) with potassium chromate and dilute sulphuric acid, separates from alcoholic solution as a crystalline powder melting at 205°–206°, slightly soluble in boiling water and in cold alcohol. Its *barium salt*, $(C^8H^6BrO^2)^2Ba + 4H^2O$, and the *calcium salt*, $(C^8H^6BrO^2)^2Ca + 3H^2O$, crystallise in needles; the *silver salt*, $C^8H^6BrO^2Ag$, is a flocculent precipitate which becomes coloured on exposure to light; the *ethylic ether* is a fragrant liquid soluble in water, boiling without decomposition at 270°–275°, and solidifying in the crystalline form at −5°. *Nitrometabromotoluic acid*, $C^8H^6(NO^2)BrO^2$, separates on adding water to the warmed solution of metabromotoluic acid in fuming nitric acid, in the flocculent state, and forms colourless crystals melting at 175°–176°; the barium salt, $[C^8H^5(NO^2)BrO^2]^2Ba + 3H^2O$, crystallises in easily soluble needles; the calcium salt, $[C^8H^5(NO^2)BrO^2]^2Ca + 3H^2O$, in warty aggregates. *Metadibromotoluic acid*, $C^8H^6Br^2O^2$, is produced, though very slowly, by oxidising dibromoxylene with chromic acid mixture. It is insoluble in cold water, and crystallises from dilute alcohol in microscopic needles melting at 185°–186°. The easily soluble barium salt, $(C^8H^5Br^2O^2)^2Ba + 9H^2O$, forms silky needles; the silver salt, $C^8H^5Br^2O^2Ag$, is an amorphous precipitate insoluble in water (Fittig, Ahrens, a. Mattheides, *Ann. Ch. Pharm.* cxlvii. 15; *Jahresb.* 1867, p. 696).

Nitrotoluic and *Amidotoluic acids* (Ahrens, *Zeitschr. f. Chem.* [2] v. 102).—Coal-tar xylene, boiling at 138°–140°, was oxidised with a mixture of 1 vol. nitric acid and 3 vol. water, and yielded a mixture of acids which, after distillation, conversion into calcium salts, and precipitation with hydrochloric acid, melted at 72°–75°. This product was gently warmed with strong nitric acid, the resulting nitro-acids precipitated by water, and, after washing, saturated with calcium carbonate.

A mixture of calcium salts differing in solubility was thus obtained, which were separated by repeated crystallisation from hot water.—A. The *nitrotoluic acid*, $C^8H^7(NO^2)O^2$, separated from the less soluble calcium salt, crystallised in large monoclinic prisms melting at 190°; its barium salt in needles containing 4 mol. water; the calcium salt in rhombic prisms with $3H^2O$; the lead salt, obtained as a precipitate, crystallised from hot water in anhydrous needles. *Amidotoluic acid*, $C^8H^7(NH^2)O^2$, formed from the preceding nitro-acid by reduction with tin and hydrochloric acid, crystallises in long, yellow, capillary needles, melting at 164°–165°. Its barium salt, $[C^8H^6(NH^2)O^2]^2Ba + 3H^2O$, is easily soluble in water; the copper, lead, and silver salts are sparingly soluble, and obtained by precipitation. *Nitroxytoluic acid*, $C^8H^6(NO^2)(OH)O^2$, formed by treating the amido-acid with nitrous acid, forms very long golden-yellow needles, soluble in water, and melting at 187°–188°. Its barium salt, $[C^8H^5(NO^2)(OH)O^2]^2Ba + 7H^2O$, is easily soluble in water, turns red when dried over sulphuric acid, and deliquesces to a lemon-yellow mass on exposure to the air.

B. The more soluble calcium salts separated from the last mother-liquor obtained as above yield a mixture of two nitrotoluic acids, one crystallising in thick monoclinic prisms melting at 220°, the other in capillary needles melting at 217°–218°; the crystalline forms of these two acids are not altered by recrystallisation. They are both insoluble in water, easily soluble in alcohol. The calcium salt of the acid melting at 220° forms well-defined tabular crystals very soluble in water.

Alphatoluic or Phenylacetic Acid. $CH^2\left\{\begin{matrix}C^6H^5\\ COOH\end{matrix}\right.$.—This acid, first obtained by Cannizzaro by boiling benzyl cyanide with potash, afterwards by Möller a. Strecker from vulpic acid by the action of baryta-water (v. 863), is also produced by heating mandelic (phenyl-glycollic) acid with concentrated hydriodic acid and a small quantity of phosphorus (Crum-Brown, *Proc. Roy. Soc. Edinb.* v. 409):

$$CH(OH)\left\{\begin{matrix}C^6H^5\\ COOH\end{matrix}\right. - O = CH^2\left\{\begin{matrix}C^6H^5\\ COOH\end{matrix}\right..$$

The *methylic ether* of alphatoluic acid, obtained by treating the acid with alcohol and hydrochloric acid, is a colourless liquid having a faint odour, a sp. gr. of 1·044 at 16°, and boiling without decomposition at 220°. The *ethylic ether*, obtained in like manner, has an unpleasant odour, a sp. gr. of 1·031, and boils at 226° (Radziszewski, *Zeitschr. f. Chem.* [2] v. 358).

Phenylbromacetic or *Bromalphatoluic acid*, $CHBr\left\{\begin{matrix}C^6H^5\\ COOH\end{matrix}\right.$, is formed by the action of hydrobromic acid on mandelic acid:

$$CH(OH)\left\{\begin{matrix}C^6H^5\\ CO^2H\end{matrix}\right. + HBr = H^2O + CHBr\left\{\begin{matrix}C^6H^5\\ CO^2H\end{matrix}\right..$$

A solution of mandelic acid in fuming hydrobromic acid yields phenyl-bromacetic acid, gradually at ordinary temperatures, more quickly when heated, in oily drops which gradually crystallise. By recrystallisation from carbon bisulphide, it is obtained in yellow prisms melting at 382°. By sodium-amalgam and water it is reduced to alphatoluic acid. Potassium hydrate added to its alcoholic solution quickly converts it into phenyl-ethyl-glycollic acid:

$$CHBr\left\{\begin{matrix}C^6H^5\\ CO^2H\end{matrix}\right. + KOC^2H^5 = KBr + CH(OC^2H^5)\left\{\begin{matrix}C^6H^5\\ CO^2H\end{matrix}\right..$$

The resulting solution filtered from potassium bromide, slightly acidulated with hydrochloric acid, then evaporated over the water-bath, and mixed with lukewarm water, leaves a yellowish oil, consisting of phenyl-ethyl-glycollic acid, which may be converted into a barium salt and separated therefrom by hydrochloric acid, in the form of a transparent, uncrystallisable, glutinous mass resembling bird-lime. Its salts are also mostly amorphous. The *barium salt* is very soluble in water, and remains as a gummy mass on evaporation in a vacuum. The *lead salt* is sparingly soluble, and becomes crystalline on standing. The *silver salt* is a white pulverulent precipitate (Glaser a. Radziszewski, *Zeitschr. f. Chem.* [2] iv. 140).

Phenylchloracetic or *Chloralphatoluic acid*, $CHCl\left\{\begin{matrix}C^6H^5\\ CO^2H\end{matrix}\right.$, is prepared by heating mandelic acid with excess of fuming hydrochloric acid to 146° in sealed tubes for two or three hours, dissolving the resulting oil in sodium carbonate, decolorising with animal charcoal, and precipitating with hydrochloric acid. It then separates as a colourless oil, which gradually solidifies, and the mother-liquor yields the same acid in white rhomboïdal tables. It is soluble in alcohol, ether, carbon bisulphide, and chloroform, slightly soluble in water, melts at 78°, and solidifies in prismatic needles. Its salts crystallise with difficulty. In dilute alcoholic solution it is easily converted by sodium-amalgam into alphatoluic acid. By boiling with excess of potash it is converted into an acid soluble in water, the barium salt of which has the form and composition of the mandelate (Radziszewski, *ibid.* v. 356).

Phenyldichloracetic acid, $CCl^2\left\{\begin{matrix}C^6H^5\\CO^2H\end{matrix}\right.$, is obtained either by the action of dry chlorine on the monochlorinated acid in sunshine, or by passing chlorine gas through the same acid in a U-tube immersed in boiling water, and purified by conversion into sodium salt and precipitation with hydrochloric acid. It then separates as an amber-coloured oil which gradually solidifies, and the remaining liquid becomes filled with square tables united in laminar groups. It melts at 69° and solidifies in crystalline scales; is slightly soluble in water, and crystallises therefrom in transparent square tables, from ether in small concentrically grouped needles. Its salts crystallise better than those of the monochlorinated acid. By dry distillation it gives off chlorine, hydrochloric acid, and a yellow oil, leaving a carbonaceous residue. By boiling with excess of potash, it is converted into an acid easily soluble in water. When it is boiled with potash till the solution no longer gives a precipitate with sulphuric acid, and then boiled with sulphuric acid and potassium dichromate, it gives off vapours smelling like bitter almond oil, and is finally converted into benzoic acid (Radziszewski, *loc. cit.*).

Parabromophenylacetic acid is formed by the action of bromine on α toluic acid. It crystallises in prisms melting at 76°; its barium and calcium salts form nodular groups of crystals easily soluble in water and alcohol. By oxidation with chromic acid mixture, it is converted into parabromobenzoic acid melting at 251°, together with another brominated acid which melts at 99°. Nitric acid converts it into parabromonitrophenylacetic acid, which crystallises in prisms. When bromine acts on *α* toluic acid at 150°, the chief product is phenylbromacetic acid, which by boiling with soda-ley is converted into mandelic acid (Radziszewski).

Paranitrophenylacetic acid, $CH(NO^2)\left\{\begin{matrix}C^6H^4\\CO^2H\end{matrix}\right.$, obtained by the action of fuming nitric acid on *α* toluic acid at ordinary temperatures, crystallises from alcohol in colourless prisms melting at 114°. Its sodium salt, $C^8H^6(NO^2)O^2Na + 2H^2O$, crystallises from alcohol in square tables. The acid saturated with ammonia forms a yellowish precipitate with silver salts, green with copper salts, white with mercurous and mercuric salts. The *ethylic ether* obtained by nitration of ethylic phenylacetate crystallises from alcohol in rhombic tables melting at 64°. The nitro-acid is converted by oxidation with chromic acid mixture into paranitrobenzoic acid, melting at 230°.

Para-amidophenylacetic acid, $CH(NH^2)\left\{\begin{matrix}C^6H^4\\CO^2H\end{matrix}\right.$, is obtained, in combination with stannous chloride, by treating the nitro-acid with tin and hydrochloric acid. When separated therefrom it crystallises in nacreous laminæ, easily decomposed by heat or by contact with moist air, insoluble in cold water, moderately soluble in warm water and in alcohol. Its *hydrochloride* forms long colourless needles, not volatile without decomposition; the *neutral sulphate* crystallises easily in six-sided tables. The *silver salt* is a white unstable precipitate; the *copper salt* is green, and quite insoluble in water.

When the mononitrated acid is reduced by ammonium sulphydrate, and the amidated acid is precipitated by acetic acid, a yellowish liquid remains, from which hydrochloric acid throws down para-azophenylacetic acid. This acid is insoluble in cold water, and crystallises from hot water in very long nacreous straw-coloured needles melting at 138°.

Dinitrophenylacetic acid is formed by treating the paranitro-acid with a mixture of nitric and sulphuric acid. It crystallises from water in thin needles melting at 160°, and easily forms ethers. Another nitro-acid is formed at the same time in small quantity (Radziszewski).

TOLUIDINE or **AMIDOTOLUENE.** $C^7H^9N = C^7H^7(NH^2) = C^6H^4\left\{\begin{matrix}CH^3\\NH^2\end{matrix}\right.$ This base exhibits the three modifications, ortho-, meta-, and para-. The crystallised base obtained by Hofmann a. Muspratt in 1840, by reduction of nitrotoluene, appears to be paratoluidine; a liquid modification lately discovered by Rosenstiehl in commercial toluidine, and named *pseudo-toluidine*, is most probably the ortho-modification; and metatoluidine may also be obtained from crude commercial toluidine (p. 1103).

On the action of light on *chloride, bromide,* and *iodide of silver*, see Poitevin, *Bull. Soc. Chim.* [2] v. 155;—Kaiser, *Jahresb.* 1865, p. 279;—Carey Lea, *Sill. Am. J.* [2] xxxix. 74; xl. 109; xlii. 198; *Jahresb.* 1865, pp. 279, 282; 1866, p. 262;—H. Vogel, *Pogg. Ann.* cxxv. 329;—W. Reissig, *J. pr. Chem.* xcv. 405;—Schultz-Sellack, *Deut. chem. Ges. Ber.* iv. 210; *Chem. Soc. J.* [2] ix. 302. According to Lea, pure silver iodide is not reduced by light, the reduction taking place only in presence of silver nitrate or organic bodies.

Silver Fluoride. AgF.—This compound has been carefully examined by Gore (*Phil. Trans.* 1870, 227; *Proc. Roy. Soc.* xix. 235). It was prepared by dissolving pure silver carbonate in hydrofluoric acid and evaporating in a platinum dish, but, unless peculiar precautions are taken, it generally contains a little metallic silver and traces of water and hydrofluoric acid. It is usually obtained in yellow earthy lumps, but when completely dehydrated by fusion, it forms a black horny mass, having a silvery lustre on the surface, arising from minute particles of metallic silver. It is extremely deliquescent; 1 pt. of it dissolves in 0·55 pts. water at 15·5°, heat being evolved in the dissolution, and a strongly alkaline liquid being formed. The saturated solution has a sp. gr. of 2·61 at 15·5°, exhibits supersaturation on cooling, and solidifies, with rise of temperature, when a platinum plate is dipped into it. Crystals of a hydrated salt may be obtained from the solution, but the rest of the salt separates at the same time in the anhydrous and amorphous state. The dry salt is not decomposed by light. It melts below a visible red heat, forming a strongly lustrous, mobile, pitch-black liquid. It is not decomposed by heat alone, but in the fused or semifused state it is quickly decomposed by the moisture of the air, with separation of metallic silver; dry air does not affect it. Brought in contact in the fused state with platinum poles, it conducts electricity like a metal, without visible evolution of gas or corrosion of the positive pole; a silver pole is quickly dissolved, and a carbon pole gradually attacked. The aqueous solution yields by electrolysis, silver crystals at the negative, and silver peroxide at the positive pole. Hydrogen does not affect the dry salt in sunshine, but decomposes it gradually at a commencing red heat, with separation of metallic silver. The dry salt and the aqueous solution are not decomposed by oxygen or by nitrogen; neither do the oxides of nitrogen act on the fused salt. Ammonia gas is quickly absorbed by the dry and by the fused salt, in the latter case with separation of metallic silver; the concentrated solution is also decomposed by strong aqueous ammonia. When vapour of hydrofluoric acid is passed over the perfectly dry and previously fused salt, at a temperature of 13°, an acid fluoride is formed, which however decomposes at a slightly higher temperature.

When silver fluoride is heated in chlorine gas, in vessels constructed partly of glass, partly of platinum, the glass is more or less attacked, the chlorine unites with the platinum and the silver fluoride, forming a double salt, $4AgCl.PtF^4$, and a vacuum is produced. Similar results are obtained in vessels of platinum alone or of gold. In vessels constructed partly of purified graphite a compound of fluorine and carbon is formed. Bromine and iodine act upon silver fluoride in a similar manner; iodine however does not form a double salt analogous to the chlorine-compound above mentioned. An aqueous solution of silver fluoride agitated with chlorine becomes hot and gives off oxygen:

$$8AgF + Cl^8 + 4H^2O = 7AgCl + AgClO^3 + 8HF + O.$$

Dry hydrochloric acid gas completely decomposes silver fluoride in the melted state, but only acts upon it superficially at 60° F. A saturated aqueous solution of silver fluoride is not precipitated by chloric acid.

Silver Oxides. *Argentous Oxide*, Ag^4O, is produced by the action of hydrogen dioxide on metallic silver (and therefore also in the decomposition of argentic oxide by excess of hydrogen dioxide). A bright silver plate immersed in a perfectly neutral solution of hydrogen dioxide becomes covered with bubbles of oxygen and coated with a greyish-white film, while part of the silver is converted by addition into hydrated argentous oxide, according to the equation $2Ag^2 + H^2O^2 = 2HAg^2O$, and dissolves in the liquid; a small quantity of a grey-black precipitate is likewise deposited. The solution of argentous hydrate when exposed to the air acquires the colour of cobaltous salts, and becomes slightly clouded by separation of finely divided silver. With potash it forms a brown-black precipitate; with hydrochloric acid a precipitate of silver chloride and metallic silver: $2HAg^2O + 2HCl = 2H^2O + 2AgCl + Ag^2$. When evaporated it leaves a residue which appears crystalline under the microscope, and when treated with water gives up argentic hydrate and deposits metallic silver in transparent, red, microscopic crystals, according to the equation $2HAg^2O = 2HAgO + Ag^2$;

Wroblevsky (*ibid.* vi. 165) has obtained two isomeric bromonitrotoluenes, and corresponding modifications of bromotoluidine. Crystallised (para-) bromotoluene was nitrated, the solution precipitated by water; the oily product, after washing and drying, was exposed to a freezing mixture; and the solidified mass subjected to strong pressure at a winter temperature. The solid product which remained did not melt at the ordinary temperature of a room. On boiling the press-cake with water, an oily product passed over, which did not solidify at −20°. The *solid* (α) bromonitrotoluene recrystallised from alcohol forms long needles, melts at 43°, and boils without decomposition at 256°–257°. The *liquid* (β) bromonitrotoluene remains liquid at −20°, has a sp. gr. of 1·631 at 18°, and boils at 255°–256°. In the solid modification the nitro-group appears to occupy the *meta-* place.

α *Bromotoluidine* prepared from the solid nitro-compound by the action of tin and hydrochloric acid is *liquid*, and solidifies at −2°. β *Bromotoluidine* prepared in like manner from the liquid nitro-compound is *solid*, crystallises in prisms, and melts at 67°. The nitrate of the α base forms beautiful nacreous crystals, soluble in 120·9 pts. water at 11·5°; the β nitrate forms prismatic crystals, soluble in 217·4 pts. water at 11·5°.

2. From *acetoluide*, $C^7H^7.NH(C^2H^3O)$ (v. 871). This compound treated under water with 2 at. bromine, and gently warmed, is converted into bromacetoluide, $C^7H^6Br.NH(C^2H^3O)$, which crystallises in needles melting at 117°, and when boiled with alcoholic potash is resolved into acetic acid and bromotoluidine. The base thus obtained boils at 220°, is insoluble in water, easily soluble in alcohol, and has a specific gravity of 1·510 at 20°. The nitrate crystallises in very fine large yellow laminæ, the hydrochloride in white nacreous prisms, the acid oxalate and acid sulphate in needles (Wroblevsky, *ibid.* v. 279).

3. Together with dibromotoluidine, by the direct action of bromine on toluidine. When 1 mol. bromine is passed, by means of a current of air, into aqueous toluidine hydrochloride, or into the alcoholic solution of free toluidine, a copious precipitate of dibromotoluidine is obtained, together with a small quantity of monobromotoluidine. The alcoholic solution is mixed with water, the precipitated dibromotoluidine separated by filtration, the acid filtrate evaporated to dryness over the water-bath as long as acid vapours continue to escape, the residue then dissolved in cold water, and the filtered solution mixed with ammonia, which throws down only monobromotoluidine. To purify this base it is converted into a crystallised salt, and this salt is decomposed by distillation with potash. The bromotoluidine thus obtained forms a hydrochloride and nitrate agreeing exactly with those of the bromotoluidine prepared from acetoluide. The nitrate is converted by nitrous acid into a diazobromotoluene, the sulphate of which decomposed by alcohol yields orthobromotoluene, C^7H^7Br, convertible by oxidation with chromic acid into orthobromobenzoic acid (Wroblevsky, *ibid.* v. 460).

Dibromotoluidine, $C^6H^2Br^2(NH^2).CH^3$, crystallises in long white silky needles melting at 73°, insoluble in water, but soluble in alcohol and ether. It does not unite with acids, is scarcely acted upon by bromine, but is strongly attacked by fuming nitric acid, apparently yielding products of oxidation (Wroblevsky).

On bromotoluidines, see further Wroblevsky (*Zeitschr. f. Chem.* [2] vii. 135, 240; *Chem. Soc. J.* [2] ix. 564, 713).

Chlorotoluidine. $C^7H^8ClN = C^6H^3Cl\left\{\begin{matrix}CH^3\\ NH^2\end{matrix}\right.$.—This base has been obtained in three modifications, two liquid at ordinary temperatures, the third solid.

1. Acetoluide suspended in water and treated with chlorine gas till the vessel shows an increase of weight corresponding to 2 at. chlorine, is converted into chloracetoluide, $C^7H^6Cl.NH(C^2H^3O)$, which crystallises in large red laminar crystals, melting at 99°, and resolved by boiling with alcoholic potash into acetic acid and chlorotoluidine. The chlorinated base thus obtained is a colourless liquid smelling like toluidine; it boils without decomposition at 222°, has a sp. gr. of 1·151 at 20°, dissolves easily in alcohol, but is nearly insoluble in water. Its salts crystallise very beautifully, the nitrate and hydrochloride in prisms, the latter subliming at 100°, the acid sulphate in prisms, the acid oxalate in long white needles (Wroblevsky, *Zeitschr. f. Chem.* [2] v. 322).

2. Parachloronitrotoluene, $C^7H^6Cl(NO^2)$, obtained by direct nitration of parachlorotoluene, is converted by tin and hydrochloric acid into a double salt $2(C^7H^6ClNH^2.HCl).SnCl^2$, from which the tin may be separated by hydrogen sulphide, leaving parachlorotoluidine hydrochloride, $C^7H^6ClNH^2.HCl$, and from this salt the (para-) chlorotoluidine may be separated by distillation with caustic soda. The chlorinated base thus obtained is a colourless, oily, strongly refracting liquid, smelling like ordinary toluidine, having a sp. gr. of 1·175 at 18°, and boiling at 236° (*i.e.* 14° higher than the preceding); it becomes coloured in contact with the air. Its hydrochloride forms very light nacreous laminæ, which may be purified by sublimation; the nitrate

crystallises in thin translucent perfectly white laminæ; the sulphate is very soluble in water (Henry a. Radziszewski, *ibid.* 542).

According to a later statement by the same authors (*ibid.* vi. 157), the chlorotoluidine obtained as above crystallises in needles, melts at 85°, and boils at 243°.

Wroblevsky (*ibid.* 683), by treating pure chlorotoluene with nitric acid of sp. gr. 1·475, and subjecting the product to fractional distillation, obtained two nitrochlorotoluenes, one (*a*) boiling at 243°, the other (*β*) at 253°, both of which remained perfectly fluid at −13°. Both of these were converted into chlorotoluidines by reduction with tin and hydrochloric acid.

a Chlorotoluidine from *a* nitrochlorotoluene is a liquid not solidifying at −14°. It is colourless, but turns brown on exposure to the air, and has a faint odour like that of toluidine. Sp. gr. 1·1855 at 20°. Boiling point 238°. Insoluble in water, easily soluble in alcohol. Its nitrate and hydrochloride crystallise in prisms, the latter subliming like sal-ammoniac.

β Chlorotoluidine is a liquid when first separated, but solidifies on standing, or more quickly when cooled. When freed from the adhering liquid modification by pressure, distillation, and crystallisation from alcohol, it forms large colourless nacreous laminæ melting at 83° and boiling at 241°. It is nearly insoluble in water, easily soluble in alcohol, and has a faint odour. Its salts crystallise remarkably well, the hydrochloride in colourless nacreous laminæ with pointed ends, subliming like sal-ammoniac, but much less soluble in water than the *a* salt; the nitrate in large shining tables melting with decomposition at 169°.

The two chlorotoluidines obtained by Wroblevsky are probably identical with those described by Henry a. Radziszewski; the second has also been obtained by Beilstein a. Kuhlberg (*ibid.* 281).

Nitrotoluidine, $C^7H^6(NO^2)(NH^2) = C^6H^3(NO^2)\left\{\begin{matrix}CH^3\\NH^2\end{matrix}\right.$, obtained by reduction of dinitrotoluene, forms broad yellow shining needles melting at 77·5°, easily soluble in hot water, very slightly in cold water. The *nitrate* forms small yellow anhydrous laminæ melting with decomposition at 185°. The *hydrochloride* forms tufts of yellow needles, or, slowly crystallised, long yellow slender needles; melts with decomposition at 220°; is moderately soluble in water, especially at the boiling heat. The *sulphate,* $[C^7H^6(NO^2)(NH^2)]^2.H^2SO^4 + 2H^2O$, pale rose-coloured needles arranged in stellate groups. The nitrate is converted by nitrous acid into *nitrate of diazonitrotoluene* $C^7H^5(NO^2)N^2.NO^3$ (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2] v. 280).

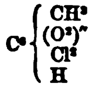
Vinyl-toluidine, $C^9H^{11}N = C^7H^6(C^2H^3).NH^2$ (Wurtz, *Compt. rend.* lxviii. 1504; *Zeitschr. f. Chem.* [2] v. 482), is produced by heating 1 mol. toluidine with 3 mol. glycolic chlorhydrin to 220°–225° for several hours. A thick brown liquid is then formed, which dissolves only partially in water, with separation of a black flocculent or resinous mass. On agitating the whole with ether, a considerable quantity of vinyl-toluidine is dissolved, part of which sometimes separates in the form of a powder which may be dissolved in ether, or better in benzol. The ethereal solution when left to evaporate yields coloured crystals of the same base, which may be purified by washing with a little ether, and recrystallisation from benzol. It then forms perfectly colourless prisms melting at 189°–191° and resolidifying at 183°; is quite insoluble in water; dissolves in moderately concentrated sulphuric and hydrochloric acid, but is reprecipitated from these solutions by water in its original state. It is therefore a very weak base, but nevertheless forms a yellow platinochloride, $2(C^9H^{11}N.HCl).PtCl^4$, when platinic chloride is added to its solution in hydrochloric acid. Vinyl-toluidine is likewise formed when toluidine is heated to 195°–205° with an equal weight of ethylene bromide, the brominated base $C^7H^7.NH(C^2H^4Br)$, which is the normal product of the reaction, being resolved into hydrobromic acid and vinyl-toluidine.

The coloured aqueous mother-liquor, from which the vinyl-toluidine has been extracted by ether or benzol, contains the hydrochlorides of two bases, $C^7H^5(C^2H^3)^2N$ and $C^7H^6(C^2H^4OH)(C^2H^3)N$, in variable proportion; the latter when predominant imparts to the liquid a deep colour and very distinct green fluorescence. These bases may be separated by fractional precipitation with platinic chloride, the platinochloride of the di-vinyl base separating out first. The *hydrochloride* of this base, $C^{11}H^{11}N.HCl$, separated from the platinochloride by hydrogen sulphide, crystallises with 1 mol. water, which is given off at 100°. Ammonia added to the solution throws down colourless oily drops. In an atmosphere of bromine the solution of the hydrochloride takes up 6 at. bromine, forming a red liquid, which evaporates over quick lime to a ruby-coloured crystalline mass.

The *platinochloride* of the other base, decomposed with hydrogen sulphide, yields a yellow solution with splendid green fluorescence, which when evaporated in a vacuum leaves a coloured crystallised mass. These crystals dissolve in alcohol, and the solution covered with a layer of ether yields the *hydrochloride*, $C^{11}H^{13}NO.HCl$, in brownish-yellow nodules. The concentrated aqueous solution of this salt is brownish-yellow, and possesses great colouring power; when diluted it turns yellow; and when very greatly diluted reflects light with a beautiful green colour. The dry hydrochloride exposed to an atmosphere saturated with bromine deliquesces to a red liquid, which solidifies over quick lime to an orange-red crystalline mass containing about 4 at. bromine to 1 mol. of the hydrochloride. The solution of the hydrochloride treated with a large excess of hydriodic acid and left to evaporate, yields crystals of the *hydriodide*, $C^{11}H^{13}NO.HI$, which when recrystallised from water forms golden-yellow laminæ; its solution is not fluorescent. With silver nitrate, this salt yields a soluble strongly fluorescent nitrate.

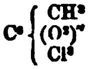
The two bases $C^{11}H^{11}N$ and $C^{11}H^{13}NO$ are not true derivatives of toluidine, inasmuch as they contain, not the radicle tolyl, C^7H^7, but toluenyl, C^7H^5. The group CH^3 in fact gives up H^2, and this hydrogen converts part of the glycolic chlorhydrin into ethyl chloride and water: $C^2H^5ClO + H^2 = C^2H^5Cl + H^2O$. The crude coloured product of the reaction contains indeed ethyl chloride, together with ethylene chloride, the latter formed according to the equation, $C^2H^5ClO + HCl = H^2O + C^2H^4Cl^2$. The hydrochloric acid required for this last reaction is supplied by the reaction of 3 mol. glycolic chlorhydrin on a single molecule of toluidine (Wurtz).

TOLUQUINONES (Graebe a. Borgmann, *Zeitschr. f. Chem.* [2] iv. 118;—Borgmann, *ibid.* vi. 122).—The di- and tri-chlorinated derivatives of the quinone of toluene are obtained by the action of potassium chlorate on cresol, just as the chlorinated quinones of the benzene series are produced from phenol. These compounds are represented by the formulæ:



$$C^6\begin{cases}CH^3\\(O^2)''\\Cl^2\\H\end{cases}$$

Dichlorotoluquinone,



$$C^6\begin{cases}CH^3\\(O^2)''\\Cl^3\end{cases}$$

Trichlorotoluquinone.

The dichlorinated compound has not been obtained pure. *Trichlorotoluquinone*, purified by repeated crystallisation from alcohol, forms yellow laminar crystals sparingly soluble in cold, more easily in boiling alcohol, easily soluble in ether and in chloroform, almost insoluble in boiling water. It sublimes with aqueous vapours, decomposes before it melts, and forms with soda-ley a red-brown solution which after a while deposits red crystals.

Trichlorotoluhydroquinone, $C^7H^5Cl^3O^2 = C^6[CH^3(OH)^2Cl^3]$, is obtained by heating tritoluchloroquinone with aqueous sulphurous acid, and recrystallising the resulting crystals from large quantities of boiling water or dilute alcohol, with addition of a little sulphurous acid. It forms colourless inodorous needles, dissolves easily in alcohol, very sparingly in water, melts at 212°, sublimes without decomposition, dissolves with red colour in ammonia or caustic soda, and in aqueous solution forms with lead salts a precipitate soluble in acetic acid. When moist it turns green on exposure to the air. Oxidising agents convert it into trichlorotoluquinone.

Diacetyl-trichlorotoluhydroquinone, $C^7H^3(C^2H^3O)^2Cl^3O^2$, is formed when trichlorotoluhydroquinone is heated to 100° for some time with excess of acetyl chloride. The resulting crystals may be purified by washing with water and dilute soda-ley and sublimation. It melts at 114°, sublimes in prismatic needles, dissolves sparingly in water, easily in alcohol and ether, is not attacked by soda-ley even when heated, but fuming nitric acid at the boiling heat slowly converts it into trichlorotoluquinone.

Diethyl-trichlorotoluhydroquinone, $C^7H^3(C^2H^5)^2Cl^3O^2$, is produced by heating trichlorotoluhydroquinone (1 mol.) to 140°–150° for four hours with potassium hydrate (2 mol.), ethyl iodide (rather more than 2 mol.), and a little alcohol, and purified by digesting the resulting crystals on the water-bath with strong soda-ley, washing with water, and sublimation. It melts at 107°, sublimes in slender needles, dissolves sparingly in water, easily in alcohol and ether, is not attacked by potash-ley.

Monochlorotoluhydro-bisulphoquinonic Acid.—The potassium salt of this acid, $C^7H^5ClO^2(SO^3K)^2$, is formed by dissolving trichlorotoluquinone at a gentle heat in concentrated aqueous potassium bisulphite, and separates after some time as a granular precipitate, which by recrystallisation from hot water is converted into white shining laminæ. It is insoluble in alcohol, slightly soluble in cold, moderately soluble in hot water, not precipitated by barium chloride. With neutral lead acetate it forms a white, with the basic acetate a yellow precipitate, both soluble in acetic acid. It dissolves in soda-ley, forming a yellow solution (Borgmann).

TOLURIC ACID. $C^{10}H^{11}NO^3$.—According to Schultzen a. Naunyn (*Zeitschr. f. Chem.* [2) iv. 29), this acid is found in the urine after xylene has been swallowed; the acid which they obtained did not however agree in its properties with that described by Kraut (v. 868), the acid itself and the barium salt being uncrystallisable. The *zinc salt*, $(C^{10}H^{10}NO^3)^2Zn + 4H^2O$, crystallised in white silvery laminæ; the copper salt, $(C^{10}H^{10}NO^3)^2Cu + 6H^2O$, in groups of blue-green needles.

TOLUYLENE or **STILBENE.** $C^{14}H^{12}$.—This hydrocarbon, discovered by Laurent (v. 431), is produced, together with tolallyl sulphide and thionessal, by the dry distillation of benzyl sulphide, benzyldisulphide, and sulphobenzide (v. 859, and *Supplement*, p. 1087).—2. Together with toluene, by heating bromotoluene with sodium:

$$4C^7H^7Br + 2Na^2 = C^{14}H^{12} + 2C^7H^8 + 4NaBr$$

(Fittig, *Ann. Ch. Pharm.* cxxxix. 178).

3. By the action of sodium on benzylene chloride at the boiling heat: $2C^7H^6Cl^2 + 2Na^2 = 4NaCl + C^{14}H^{12}$ (Limpricht, *ibid.* 303).—4. By heating bitter almond oil with sodium:

$$2C^7H^6O + 2Na^2 = 2Na^2O + C^{14}H^{12}.$$

On distilling the product, the portion which goes over at 265° consists almost wholly of toluylene (C. Gr. Williams, *Chem. News*, xv. 244).

Toluylene crystallises in nacreous plates, as observed by Laurent (v. 431). It melts at 119·5° (Limpricht), at 120° (Fittig; Williams). Vapour-density = 6·024 (Williams); calc. for $C^{14}H^{12}$ = 6·228.

Toluylene heated for eight hours to 140°–150°, with concentrated *hydriodic acid*, is converted, by addition of hydrogen, into dibenzyl, $C^{14}H^{14}$, which separates from alcohol in crystals melting at 48°–50°. By similar treatment with hydrobromic acid, toluylene suffers no alteration. In *fuming sulphuric acid* it dissolves, with formation of a non-crystallisable sulpho-acid, whose barium salt, $C^{14}H^{10}BaS^2O^6$, is separated from aqueous solution by alcohol, as a yellowish amorphous precipitate.

With *nitric acid* toluylene forms resinous, difficultly crystallisable nitro-products, one of which separated from the ethereal solution, on addition of alcohol, in yellow nodules melting at 180°, and having approximately the composition $C^{14}H^{10}(NO^2)^2$. This compound was reduced by tin and hydrochloric acid to an unstable, insoluble base crystallising in needles and represented approximately by the formula $C^{14}H^{10}(NH^2)^2$ (Märcker, *Ann. Ch. Pharm.* cxl. 86).

Toluylene Bromide,[*] $C^{14}H^{12}Br^2$, separates almost completely on mixing a solution of toluylene in ether or carbon bisulphide with bromine, whilst substitution-products (*e.g.* $C^{14}H^{11}Br$) remain in solution. The bromide, after washing with ether, and boiling with strong alcohol, consists of small silky needles, slightly soluble in boiling absolute alcohol, rather more soluble in ether and carbon bisulphide, moderately soluble in hot xylene, melting at 230°–235°, and resolved by distillation at a higher temperature into bromine, hydrobromic acid, toluylene, and monobromotoluylene, $C^{14}H^{11}Br$. Heated to 130° for some hours with *alcoholic potash*, it is converted into monobromotoluylene, which latter is further partially converted at the same time, or completely by 10 to 12 hours' heating to 130° into tolane, $C^{14}H^{10}$ (p. 1099). Toluylene bromide heated with *ammonia* to 150° for eight hours, or with aniline to 130° for twelve hours, is reconverted into toluylene. Heated with *water* to 150°, it yields, besides hydrobromic acid and toluylene, a body, $C^{14}H^{10}O^2$ (probably benzile), which crystallises in four-sided needles, melts at 95°, and volatilises without decomposition. Toluylene bromide heated with dry *silver oxide* and xylene to 140°, or with alcohol to 150°, yields, together with toluylene, an oily body having the composition $C^{28}H^{24}O^2$. By *hydriodic acid* toluylene bromide is converted into dibenzyl, by alcohol and sodium-amalgam into toluylene and dibenzyl (Limpricht a. Schwanert, *Ann. Ch. Pharm.* cxlv. 330).

Monobromotoluylene, $C^{14}H^{11}Br$, is a light yellow oily liquid, soluble in alcohol and ether, and partially decomposed by distillation. *Bromotoluylene bromide*, $C^{14}H^{11}Br^3 = C^{14}H^{11}Br.Br^2$, formed on mixing the ethereal solution of bromotoluene with bromine, crystallises in white needles, slightly soluble in cold, easily in hot alcohol and in ether, melting at 100°, and resolved by distillation into bromine, hydrobromic acid, tolane, $C^{14}H^{10}$, and tolane bromide, $C^{14}H^{10}Br^2$:

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[*] This compound was likewise obtained by Märcker (*Jahresb.* 1866, p. 600), who however regarded it as $C^{14}H^{10}Br^2$.

$$C^{14}H^{11}Br^3 = C^{14}H^{10}Br^2 + HBr$$

and

$$C^{14}H^{11}Br^3 = C^{14}H^{10} + HBr + Br^2.$$

The alcoholic solution of bromotoluene bromide mixed with silver nitrate immediately yields silver bromide; heated with alcoholic soda-solution, it yields tolane, and with water at 140°, tolane bromide.

Toluylene Acetate, $C^{14}H^{12}(C^2H^3O^2)^2$, is formed by heating 1 mol. toluylene bromide and 2 mol. silver acetate for four hours to 130° with glacial acetic acid, as an oil precipitable by water, and solidifying to a crystalline mass. From xylene mixed with a little alcohol, it crystallises in warty crusts melting at 120°. The *oxalate* is formed as a resinous uncrystallisable mass by heating toluylene bromide dissolved in xylene with silver oxalate.

Toluylene Alcohol, $C^{14}H^{14}O^2 = C^{14}H^{12}(HO)^2$, identical with hydrobenzoïn (p. 332), is obtained by heating toluylene acetate with alcoholic potash or the oxalate with alcoholic ammonia. It separates from alcohol or ether by spontaneous evaporation in rather large solid crystals, which soften at 112°, and melt completely at 122°. Nitric acid converts it into benzoin, $C^{14}H^{12}O^2$.

Toluylenic Ether or **Toluylene Oxide,** $C^{14}H^{12}O$, probably identical with deoxybenzoïn (p. 332), was once obtained by heating toluylene acetate to 120° with alcoholic potash, and crystallised from alcohol in large very flat needles melting at 55° (Limpricht a. Schwanert).

TOLYL. $C^7C^7 = C^6H^4(CH^3)$.—A radicle isomeric with benzyl, $CH^2(C^6H^5)$, the former being methylated phenyl, the latter phenylated methyl. The difference of structure of these radicles in the free state may be represented by the following formulæ:

$$\underset{\text{Ditolyl.}}{C^6H^4\left\{\begin{matrix}CH^3\\ C^6H^4(CH^3)\end{matrix}\right.} \qquad\qquad \underset{\text{Dibenzyl.}}{CH^2\left\{\begin{matrix}C^6H^5\\ CH^2(C^6H^5)\end{matrix}\right.}$$

TOLYL ACETATE appears to be formed, as a liquid having an agreeable odour, by heating monochloroxylene with silver acetate (Lauth a. Grimaux, *Bull. Soc. Chim.* [2] vii. 233).

TOLYL ALDEHYDE, $C^8H^8O = C^7H^7.CHO = C^6H^4\left\{\begin{matrix}CH^3\\ CHO\end{matrix}\right.$, is produced by heating monochloroxylene, $C^6H^4\left\{\begin{matrix}CH^3\\ CH^2Cl\end{matrix}\right.$, with ½ mol. lead nitrate and 6 or 7 pts. of water, as a liquid smelling like bitter almond oil and cinnamon oil, boiling at 200°, and capable of uniting with acid sodium sulphite.

TOLYL-FORMAMIDE. *Pseudotolyl formamide*, $N(CHO.C^7H^7.H)$, obtained by dry distillation of pseudotoluidine formate, crystallises in nacreous laminæ, slightly soluble in water, easily in a solution of pseudotoluidine formate. It melts at 50°, solidifies again at 80°, and is resolved by dry distillation, or by heating with phosphoric anhydride, fused calcium chloride, or fuming hydriodic acid, into carbon monoxide and pseudotoluidine (Rosenstiehl, *Zeitschr. f. Chem.* [2] v. 189).

TOPAZ. Analyses of this mineral from various localities, by Rammelsberg (*Berl. Akad. Ber.* 1865, p. 264; *J. pr. Chem.* xcvi. 7; *Jahresb.* 1865, p. 894), confirm the formula $Al^2F^6.SiF^4 + 5(Al^2O^3.SiO^2)$ previously assigned to it by the same chemist (v. 875). See also Städeler (*J. pr. Chem.* xcix. 65; *Jahresb.* 1866, p. 942).

TORMENTIL (Rembold, *Ann. Ch. Pharm.* cxlv. 5).—The root of *Potentilla Tormentilla* contains, together with a little ellagic acid, a large quantity of quinovic acid, and a tannin which is resolved by acids into tormentil-red and sugar. When the aqueous decoction of the root is precipitated with neutral lead acetate, the washed precipitate decomposed under warm water with hydrogen sulphide, and the somewhat concentrated liquid mixed with neutral and basic lead acetate successively, two precipitates are obtained, the first of which, *a*, is pale red, the second, *b*, nearly white. These precipitates, when well washed and again decomposed, yield corresponding liquids, A and B. The red-brown liquid, A (which does not give up to ether either gallic acid or any other crystalline body), deposits, when boiled for several hours with dilute sulphuric acid, red-brown, amorphous tormentil-red, together with a little quinovic acid. The liquid filtered therefrom contains a sugar which, after purification, forms a honey-yellow syrup having the composition $C^6H^{12}O^6$.

When the extract-like evaporation-residue of the liquid A is boiled for some hours with strong potash-ley, and the resulting mass is supersaturated with sulphuric acid, ether extracts from it ellagic acid (slightly soluble in water), and a crystalline body precipitable by neutral lead acetate (perhaps impure protocatechuic acid), turned blue and afterwards green by ferric chloride.

The tormentil-red obtained as above is separated from the quinovic acid by treatment with baryta-water; the brown insoluble compound separated by filtration from the dissolved barium quinovate is decomposed while yet moist by hydrochloric acid; and the washed residue is dissolved in dilute ammonia and again decomposed with hydrochloric acid. Tormentil-red is thus obtained as a red-brown, amorphous precipitate resembling phlobaphene in its chemical relations. It has the same composition as ratanhia-red or chestnut-red, and is probably identical therewith, inasmuch as it is resolved by oxidation with potassium hydrate into protocatechuic acid and phloroglucin.

The liquid B, obtained from the lead-precipitate *b*, is nearly colourless, and when carefully evaporated leaves yellow-reddish amorphous tormentil tannin, having, when dried at 120°, the composition $C^{26}H^{22}O^{11}$. When boiled with dilute sulphuric acid, it is converted, like chestnut-tannin, without sensible formation of sugar, into tormentil-red, which has nearly the same composition. Tormentil-tannin precipitates solution of gelatin, and gives with ferric chloride a blue-green coloration, changing to violet-red on addition of sodium carbonate. The sugar formed by boiling the liquid A with sulphuric acid appears to be produced chiefly from the quinovin, which is resolvable into sugar and quinovic acid.

The quinovic acid, $C^{24}H^{38}O^4$, is obtained in rather large quantity, by twice boiling the tormentil root with thin milk of lime, acidulating the filtrate, boiling the washed precipitate with baryta-water, and again precipitating the filtered solution with hydrochloric acid. The washed precipitate is dissolved in a large quantity of hot alcohol, the reddish solution decolorised with animal charcoal, and part of the alcohol is distilled off; the pure quinovic acid then separates as a colourless, sandy, crystalline powder.

TOURMALINE (Rammelsberg, *Deut. chem. Ges.* 1869, p. 349; *Zeitschr. f. Chem.* [2] v. 568).—The tourmalines form an isomorphous group containing the following elements:

Univalent: H, K, Na, Li — F
Bivalent: Mg, Ca, Mn, Fe — O
Quadrivalent: Si
Tri- and Sexvalent: B and All.*

Each individual tourmaline is a molecularly isomorphous mixture of analogously constituted primary compounds. There are tourmalines not containing Li or Fe, Mn, Ca. The colourless or pale red variety from Elba contains 0·2 p. c.; the brown variety from Windisch-Kappel contains 11·8 p. c. MgO. Black tourmaline from Andreasberg contains 17·4 p. c. FeO. These qualitative and quantitative differences show themselves in the colour of the mineral: magnesium tourmalines are yellow or brown; magnesium-iron tourmalines dark brown to black; iron tourmalines black; manganese tourmalines free from iron are red, reddish, or colourless, &c. But, notwithstanding the very great variety in the individual constituents, the constitution of the tourmalines, viewed as a group, is governed by a very simple law. This law, deduced from the examination of 32 varieties, is as follows: *Tourmalines are tribasic silicates* (*Drittelsilicate*). The primary compounds may always be reduced to the following silicates:

$$\acute{R}^6SiO^5 \qquad \acute{\acute{R}}^3SiO^5 \qquad \overset{vi}{R}SiO^5$$

or

$$3\acute{R}^2O.SiO^2 \qquad 3\acute{\acute{R}}O.SiO^2 \qquad R^{vi}O^3\,SiO^2.$$

The tourmaline group resolves itself into two great divisions. In the first division the atomic ratio All : Si = 1 : 2; in the second = 2 : 3.

Tourmalines of the first division consist of tribasic silicates represented by the formulæ $\acute{R}^3AllBSi^2O^{10}$ and $\acute{\acute{R}}^3All^2B^2Si^4O^{20}$. This is the most numerous division, and to it belong 25 of the tourmalines examined by Rammelsberg. They yield 30–32 p. c. alumina. Their structure is determined by the proportion of the two silicate molecules above mentioned, and it is found that the simpler ratio 1 : 1, in which R″ : All = 1 : 1

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* All = Al^2 = 54·8.

greatly predominates, having been observed in 21 representatives; and, besides these, the relation 5 : 2, that is $\overset{\prime\prime}{R}$: All = 2 : 3, has been found in only four others (from Saar, Elba, Sarapulsk, Goshen).

Tourmalines of the second division consist of the tribasic silicate-molecules $\overset{\prime}{R}{}^{6}\mathrm{All}^{6}\mathrm{B}^{4}\mathrm{Si}^{9}\mathrm{O}^{45}$ and $\overset{\prime\prime}{R}{}^{3}\mathrm{All}^{6}\mathrm{B}^{4}\mathrm{Si}^{9}\mathrm{O}^{45}$. These tourmalines, even in entire crystals, are transparent, colourless, or slightly greenish or reddish, or red (precious tourmalines). They yield 42–44 p. c. alumina, and are nearly or quite free from iron; and, inasmuch as they contain but little manganese or magnesium, the silicate containing $\overset{\prime}{R}$ predominates in this case also over that which contains $\overset{\prime\prime}{R}$. The atomic ratio $\overset{\prime\prime}{R}$: All = 1 : 6 (Elba, pale green; Schaitansk, red); or 1 : 12 (Rozena, Paris, red); or 1 : 24 (Elba, pale red and colourless) indicates in these five varieties a variable proportion between the two silicate-molecules, viz. (2 : 1; 5 : 1; and 11 : 1).

Between these two divisions, that is to say, with an intermediate proportion of Al : Si, lies the dark green tourmaline from Brazil, and the similar one from Chesterfield. In other respects, these varieties containing 6 p. c. FeO conform to the general law; they may be regarded as forming a third division, or as being made up of isomorphous mixtures of the other two. The latter view is that which Rammelsberg prefers; for it not unfrequently happens that the colours exhibited by an individual tourmaline crystal show that it is formed above and below, or externally and internally, of constituents which are chemically dissimilar, although analogous and isomorphous.

TRIDYMITE. A crystallised variety of silica occurring in clefts and cavities of a trachytic porphyry near Pachuca in Mexico. It forms hexagonal crystals, often in twins, and having a sp. gr. of 2·326 to 2·295 at 15° to 16°, which is that usually assigned to amorphous silica. The crystals are colourless, and have a vitreous to nacreous lustre, which, however, they lose by contact with the air (G. vom Rath, *Zeitschr. f. Chem.* [2] v. 410).

TRIETHYLSULPHINE CYANIDE, $S^{iv}\left\{\begin{matrix}(C^2H^5)^3\\ CN\end{matrix}\right.$, is produced by digesting the corresponding iodide (v. 611) at 100° with potassium cyanide. It remains, on evaporating the alcoholic solution, as a thick syrup, which by slow evaporation over oil of vitriol yields colourless, very deliquescent needles. Heated with acids or alkalis it is resolved, with addition of the elements of water, into ethyl sulphide, propionic acid, and ammonia; also when heated with water or alcohol to 120° (Gauhe, *Zeitschr. f. Chem.* [2] iv. 622).

TRIGLYCOLLAMIC ACID. See Glycollamic Acids (p. 646).

TRIMESIC ACID.
TRIMELLITIC ACID. } See Mellitic Acid (pp. 811, 813).

TROPIC ACID. See Atropic Acid (p. 249).

TUNGSTEN. The following observations on the hydrates of tungstic acid have been made by Zettnow (*Pogg. Ann.* cxxx. 16, 240; *Bull. Soc. Chim.* [2] viii. 37, 174; *Jahresb.* 1867, 223). Tungstic acid separated from sodium tungstate by mineral acids at ordinary temperatures is soluble in ammonia. A hydrate only slightly soluble in ammonia, but easily soluble in sodium carbonate, is obtained by boiling 1½ pt. neutral or 3 pts. of the acid sodium tungstate with 1 pt. of strong sulphuric mixed with a little nitric acid, till the sulphuric acid begins to evaporate; then diluting with water; washing with water, mixed towards the end of the operation with a little sulphuric acid (to prevent the tungstic acid from running through the filter); and again heating the residue with strong sulphuric acid till the latter evaporates. The washed and air-dried tungstic acid has a light lemon-yellow colour with a tinge of green:

After drying at	50°	120°–130°	200°
It contains .	3·7	2·5	1·7 p. c. water
or	$2WO^3.H^2O$	$3WO^3.H^2O$	$4WO^3.H^2O$.

When ignited, it acquires a lighter colour.

The solution of sodium monotungstate is not precipitated by sulphurous, hydriodic, hydrocyanic, oxalic, or tartaric acid; but these acids do not hinder the precipitation by mineral acids. When the solution of a tungstate is heated with acetic acid, mineral acids (as in presence of phosphoric acid) do not produce a precipitate, unless the solution has been previously neutralised with ammonia. Solutions containing 1 pt. tungstic anhydride in 10,000 pts. still give a trace of blue colour with zinc and sulphuric acid, but are not precipitated or clouded by potassium ferrocyanide, lead acetate, or stannous chloride. Solutions containing 0·005 p. c. tungstic anhydride also give with these last-mentioned reagents only a slight reaction, and at twice that degree of dilution no visible reaction occurs (lead acetate alone still produces opalescence).

For the estimation of tungstic acid in soluble neutral tungstates, Zettnow acidulates the solution with acetic acid, and precipitates it at the boiling heat with a one-tenth normal solution of lead acetate. The precipitate of neutral lead tungstate, $PbWO^4$, separates quickly towards the end of the precipitation and becomes heavy and crystalline; the end of the experiment may therefore be recognised with certainty by testing a filtered sample. Soluble acid salts must be previously converted into neutral salts by addition of sodium carbonate, and then slightly supersaturated with acetic acid; insoluble salts must be decomposed by fusion with sodium carbonate.

Zettnow has also made observations on the composition and properties of several metallic tungstates, and on the properties of metallic tungsten prepared by various processes. Observations on the tungstates have also been published by Ullik (*J. pr. Chem.* ciii. 147; *Jahresb.* 1867, p. 221).

TURACIN. A red pigment found in the wing-feathers of four species of *Turaco*. It is extracted by dilute alkalis, and may be precipitated from the solution by acids without alteration. It differs from all other known animal pigments, in the circumstance that it contains 5·9 p. c. copper, which cannot be separated without destruction of the pigment. The spectrum of this pigment exhibits two black absorption-bands. It is constant in composition, even when obtained from birds of different genus and species, as, for example, from *Musophaga violacea*, *Carythaix albo-cristata*, and *C. porphyreolopha* (Church, *Chem. News*, xix. 265; *Gmelin's Handbook*, xviii. 420).

TURPENTINE-OIL. $C^{10}H^{16}$.—Vapour of turpentine-oil passed through a red-hot iron tube filled with fragments of porcelain, is resolved into a large number of hydrocarbons, very difficult to separate, some of which are isomeric with it (Hlasiwetz a. Hinterberger, *Zeitschr. f. Chem.* [2] iv. 380).

Turpentine-oil is easily oxidised by *potassium permanganate*. 10 pts. freshly rectified turpentine-oil agitated with 500 pts. water reduce in a few hours 28 parts of the permanganate (corresponding with the proportion $C^{10}H^{16} : O^4$), if the latter be gradually added and rise of temperature avoided; the further oxidation takes place slowly at the boiling heat. The products are: 1. An acid separated from the concentrated aqueous solution by mineral acids as a resinous body easily soluble in hot water.—2. A small quantity of a neutral volatile substance which, when the aqueous mixture is distilled, sublimes in short needles having the odour of camphor, and appearing to be either camphor, $C^{10}H^{16}O$, or a body isomeric with it (Berthelot, *Bull. Soc. Chim.* [2] vii. 135).

When turpentine-oil is gradually added to a dilute solution of *hypochlorous acid*, a yellow viscid liquid is deposited (probably a mixture of di- and tri-chlorinated turpentine-oil), whilst the aqueous solution agitated with ether gives up to that liquid a neutral syrupy substance, having the composition of the dichlorhydrin of turpentine-oil, $C^{10}H^{18}Cl^2O^2$. This compound dissolves slightly in water, easily in alcohol and ether; is partly decomposed by distillation; is not resinised by nitric acid; and is converted by the action of sodium on its ethereal solution into an acid which appears to have the composition $C^{10}H^{16}O^3$ (C. G. Wheeler, *Bull. Soc. Chim.* [2] x. 288).

Turpentine-oil heated with *hydriodic acid* yields: 1. Camphene hydride, $C^{10}H^{16}.H^2$, analogous to the hydrochloride, $C^{10}H^{16}.HCl$, a liquid which boils at about 165°, is not attacked by ordinary sulphuric in the cold, and dissolves in fuming nitric acid without oxidation, yielding a nitro-compound, also in lukewarm fuming sulphuric acid, forming a sulpho-acid soluble in water; it forms a crystalline derivative with bromine.—2. Terpilene hydride, $C^{10}H^{16}.H^2H^2$, corresponding to the dihydrochloride, $C^{10}H^{16}.2HCl$, a liquid boiling at 170°–175°, difficult to separate from the preceding, not completely soluble in fuming sulphuric acid. On adding water to the mixture, a viscid product (perhaps a polymeride) separates, having the odour of camphor.—3. A saturated hydrocarbon, $C^{10}H^{22}$, which boils between 155° and 160°; withstands the action of bromine, sulphuric acid, nitric acid, &c.—4. Amyl-hydride or quintane, C^5H^{12} (Berthelot, *Compt. rend.* lxvii. 327).

A hydrocarbon isomeric with turpentine-oil is formed by the decomposition of rutylene bromide (produced from diamylene, iv. 141) with alcoholic potash. It is a transparent colourless liquid, agreeing nearly in composition with the formula $C^{10}H^{16}$, and having a vapour-density = 4·32 (calc. 4·70); but it is extremely difficult to purify. It has a strong odour of turpentine, especially when exposed to the air; burns, when set on fire, with a luminous but smoky flame. When bromine is dropped into it at −17°, the first drops unite without evolution of hydrobromic acid; but on adding a larger quantity, a violent action takes place, and hydrobromic acid is evolved. Iodine acts in a similar manner, but less strongly. Nitric acid exerts a violent oxidising action, and sulphuric acid dissolves the substance with deep brown colour. Hydrochloric acid in the gaseous state or in aqueous solution unites with it at ordinary temperatures. When the gas was passed through it for several hours at 10°, and the liquid was afterwards washed, dried, and fractionally distilled, the portion distilling between 180° and 200° decomposed with blackening and copious evolution of hydrochloric acid; and at about 110° a nearly colourless liquid distilled over, smelling of hydrochloric acid, and having nearly the composition $2C^{10}H^{16}.HCl$. The formation of this hydrocarbon from amylene may be represented by the following equations:

$$\begin{aligned} C^5H^{10} \quad + C^5H^{10} &= C^{10}H^{20} \\ C^{10}H^{20}Br^2 + 2KHO &= 2KBr + 2H^2O + C^{10}H^{18} \\ C^{10}H^{18}Br^2 + 2KHO &= 2KBr + 2H^2O + C^{10}H^{16}. \end{aligned}$$

The hydrocarbon, $C^{10}H^{16}$, thus obtained, is probably terebene (Bauer a. Verson, *Ann. Ch. Pharm.* cli. 52).

Tawildarow (*Zeitschr. f. Chem.* [2] iv. 278) has found, in the portion of coal-tar oil boiling between 172° and 190°, a hydrocarbon having nearly the composition of a lower homologue of turpentine-oil, C^9H^{14} (*nonone* according to Hofman's nomenclature, p. 794), which is acted upon by bromine, with evolution of hydrobromic acid, and formation of the compound $C^9H^{13}Br^3$ or $C^9H^{13}Br.Br^2$.

TYROSINE. $C^9H^{11}NO^3$ (Thudichum a. Wanklyn, *Chem. Soc. J.* [2] vii. 277).—When tyrosine is treated with potassium dichromate and dilute sulphuric acid (2 grms. tyrosine, less than 10 grms. sulphuric acid, 100 c. c. water and 8 grms. dichromate), carbon dioxide is evolved, together with an odour of formic acid, and an insoluble yellow-green chrome-compound is formed, consisting of $C^9H^{11}NO^{12}.Cr^2O^3.3H^2O$. This compound is nearly insoluble in water, but dissolves slowly and without evolution of gas in hydrochloric acid. When heated, it swells up, gives off carbon dioxide and water, and leaves a mixture of chromic oxide and finely divided charcoal. This compound is formed only when a small quantity of sulphuric acid is used. With excess of sulphuric acid, the only products are carbon dioxide and water, with a little formic acid.

Tyrosine boiled with a mixture of *mercuric* and *mercurous nitrates* (containing some mercurous nitrite) forms a deep red precipitate having the composition $C^9H^9(NO^2)^2NO^3Hg^2$. The mercurous salt does not take part directly in the formation of this precipitate; the entire quantity of the mercury belonging to it remains in the solution, and the function of this salt is merely to supply nitrous acid, or perhaps nitrogen dioxide. If the quantity of mercurous salt added is insufficient for this purpose, only a light flesh-coloured precipitate is formed; and when tyrosine is boiled with mercuric nitrate free from mercurous salt, and nitrogen dioxide is passed into the boiling liquid, the deep red precipitate is instantly formed (compare v. 932; also L. Meyer, *Ann. Ch. Pharm.* cxxxii. 156). This compound is very energetically attacked by alkalis, potash and ammonia forming with it a deep red solution which deposits a precipitate resembling sepia. Nitric acid dissolves the red compound, forming a red solution.

Städeler found that nitrotyrosine treated with nitric acid is converted into dinitrotyrosine (v. 934). Thudichum a. Wanklyn, however, find that this dinitro-compound is not produced, but that a nitrotyrosic acid, $C^9H^{10}(NO^2)NO^4$, is obtained, which when dissolved in water and neutralised with calcium carbonate, forms a deep red solution yielding orange-red tabular crystals, which have nearly the composition $C^9H^8Ca''(NO^2)NO^4 + 3H^2O$. If the action of the nitric acid be carried further, oxalic acid is produced.

According to Städeler, also, dinitrotyrosine is formed by the action of nitrous acid upon tyrosine. Thudichum and Wanklyn's experiments do not confirm this result. When nitrous acid (from nitric acid and arsenious oxide) is passed into water in which tyrosine is suspended, the tyrosine gradually dissolves, with yellow colour and slight evolution of gas; and on neutralising this solution with calcium carbonate, evaporating over oil of vitriol, filtering to remove a brown scum, and mixing the filtrate with lead acetate, a chocolate-coloured precipitate is formed having (at 110°) nearly the composition $C^9H^7Pb''NO^5$.

Tyrosine is not acted upon by excess of ethyl iodide at 100°; neither is it reduced by hydriodic acid at 130°.

Constitution of Tyrosine.—The nitrogen in tyrosine may be estimated by Will a. Varrentrapp's process; consequently tyrosine does not contain any nitrogen in the form of nitryl; neither is the nitrogen in the form of amidogen or imidogen, since ethyl iodide effects no substitution. The nitrogen must therefore be altogether in direct union with the carbon. Moreover there is no hydroxyl; otherwise hydriodic acid would effect a reduction; therefore the oxygen must be in direct and complete union with the carbon. Tyrosine appears to be derived from nonane, C^9H^{20}, by substitution to a considerable extent, 3 at. hydrogen having been replaced by N''', and 6 at. hydrogen by 3 at. oxygen. Its constitutional formula is most probably

$$N'''C.CH^2.CH^2.CH^2.CH^2.CH^2.CO.CO.C\left\{\begin{matrix}O\\H\end{matrix}\right..$$

Its great stability shows that the grouping of the oxygen-atoms is regular. The fact that tyrosine gives no acetic acid by oxidation, shows that it does not contain ethyl in union with part of the nitrogen or with oxygen. The easy formation of carbonic acid is in harmony with the supposition that the molecule of tyrosine contains 3 mol. carbon monoxide (Thudichum a. Wanklyn; see also Hüfner, *Zeitschr. f. Chem.* [2] iv. 391).

Tyrosine heated with fuming hydriodic acid takes up 1 mol. hydrogen, and is resolved into ammonia, which appears as ammonium iodide and phloretic acid: $C^9H^{11}NO^3 + H^2 = NH^3 + C^9H^{10}O^3$: hence Hüfner (*Zeitschr.* iv. 391) regards it as amidophloretic acid, $C^9H^9(NH^2)O^3 = C^6H^3\left\{\begin{matrix}OH\\NH^2\\C^3H^4O^2\end{matrix}\right.$. Barth, who formerly regarded tyrosine as ethyl-amidoparaoxybenzoic acid (v. 932), now regards it as oxyphenyl-amidopropionic acid, $C^2H^3\left\{\begin{matrix}C^6H^4OH\\NH^2\\COOH\end{matrix}\right.$ (*Zeitschr.* vi. 113).

Tyrosine Platinochloride, $2(C^9H^{11}NO^3.HCl).PtCl^4$, is obtained in small granular crystals, by adding the hydrochloride to a slightly acid solution of platinic chloride, and leaving the solution to evaporate in a vacuum over quick lime and fragments of calcium chloride (Gintl, *ibid.* v. 704).

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ULTRAMARINE. On the constitution of Ultramarine see W. Stein (*J. pr. Chem.* [2] iii. 39; *Chem. Soc. J.* [2] ix. 166); on the preparation of ultramarine paper, and its uses as a reagent, W. Stein (*J. pr. Chem.* ciii. 172; *Zeitschr. f. Chem.* [2] iv. 599).

URANIUM. The following method of preparing fused metallic uranium, devised by Valenciennes, is described by Peligot (*Compt. rend.* lxvii. 507). A mixture of 75 grams uranous chloride, 150 grams dry potassium chloride, and 50 grams sodium cut into pieces, is placed in a crucible and covered with potassium chloride; and this crucible is enclosed in a larger one, the space between them being packed with charcoal powder. The whole is heated in an air-furnace, and when the reaction has taken place at a red heat, the fire is strongly urged, so as to melt the metal but without volatilising the flux. The reduced uranium is found within the black very dense slag, and may be separated by lixiviation. For the success of the preparation, it is essential to exclude the moisture of the air, which would convert the uranous chloride into irreducible uranic oxide; also to protect the metal from access of air during cooling. Uranium thus prepared has a sp. gr. of 18·33.

According to Souchay (*Zeitschr. anal. Chem.* vi. 400) the precipitate formed by boiling solutions of uranic salts supersaturated with ammonium carbonate, contains in 100 pts.:

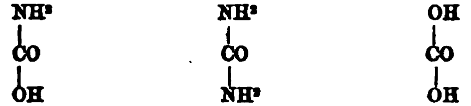
U^2O^3	CO^2	NH^3	H^2O
83·31	2·56	2·56	11·57

UREA. CH^4N^2O. The constitution of this body has lately been the subject of considerable discussion.

Basarow (*Chem. Soc. J.* [2] vi. 194) finds that urea is produced when dry ammonium carbamate, $CO^2N^2H^6$ (prepared by passing dry carbon dioxide and ammonia gases into absolute alcohol) is heated to 130°–140° in sealed tubes; also by heating the commercial carbonate of ammonia (which appears therefore to contain carbamate) to the same temperature. Conversely, Bunte, has lately shown (*Ann. Ch. Pharm.* cli. 181) that urea may be converted into ammonium carbamate (urethane) by heating nitrate of urea with alcohol:

$$\underset{\text{Urea.}}{CON^2H^4} + \underset{\text{Alcohol.}}{C^2H^5(OH)} = NH^3 + \underset{\text{Urethane.}}{CO(NH^2)(OC^2H^5)}.$$

These reactions show that urea is the amide of carbamic acid, a view advocated by Kolbe (*Zeitschr. f. Chem.* [2] iii. 50), and formerly by Heintz (*Ann. Ch. Pharm.* cxl. 276). If, however, carbamic acid be represented by the formula $H^2N—CO—OH$, its amide must be the same as the diamide of carbonic acid, that is to say, urea regarded as the amide of carbamic acid must be identical with carbamide:

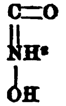


$$\begin{matrix} NH^2 \\ | \\ CO \\ | \\ OH \end{matrix} \qquad \begin{matrix} NH^2 \\ | \\ CO \\ | \\ NH^2 \end{matrix} \qquad \begin{matrix} OH \\ | \\ CO \\ | \\ OH \end{matrix}$$

Carbamic acid. Urea. Carbonic acid.

But if carbamic acid has the constitution represented by the formula

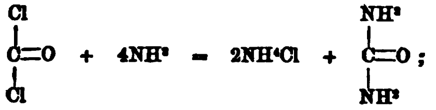
$$N^v\left\{\begin{matrix}(CO)'' \\ H^2 \\ OH\end{matrix}\right. \qquad \text{or}$$



$$\begin{matrix} C=O \\ \| \\ NH^2 \\ | \\ OH \end{matrix}$$

in which the nitrogen is quinquivalent, then its amide, urea, will have a structure different from that of carbamide, viz. $CO=NH^2—NH^2$.

With regard to this question, Heintz observes (*Ann. Ch. Pharm.* cl. 73) that the representation of carbamic acid by the formula $\left\{\begin{matrix}NH^2 \\ CO \\ OH\end{matrix}\right.$, and of amic acids in general by $\left\{\begin{matrix}NH^2 \\ R'' \\ OH\end{matrix}\right.$, or still more generally by $\left\{\begin{matrix}(NH^2)^{n-p} \\ R^{(n)} \\ (OH)^p\end{matrix}\right.$, is in accordance with the fact that such acids are never formed from monatomic, but only from polyatomic acids, whereas if the molecule were held together, not by the acid radicle, but by the nitrogen as represented by the formula, $\left\{\begin{matrix}R'' \\ NH^2 \\ OH\end{matrix}\right.$, the existence of compounds like $\left\{\begin{matrix}R'H \\ NH^2 \\ OH\end{matrix}\right.$, or $\left\{\begin{matrix}R'R' \\ NH^2 \\ OH\end{matrix}\right.$, would also be possible. Moreover the representation of urea as carbamide is in accordance with all its synthetical modes of formation, excepting those in which a transposition of the atoms must be supposed to take place—such as its formation from ammonium cyanate—which throw no light on its structure. The conversion of carbonyl chloride into urea by the action of ammonia is easily intelligible if urea be regarded as carbamide; for

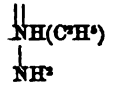


$$\begin{matrix} Cl \\ | \\ C=O \\ | \\ Cl \end{matrix} + 4NH^3 = 2NH^4Cl + \begin{matrix} NH^2 \\ | \\ C=O \\ | \\ NH^2 \end{matrix};$$

whereas if urea has the construction represented by the formula $CO—NH^2—NH^2$, its formation in the manner just mentioned involves a transposition of the atoms; but it is not easy to see why such a transposition should take place, inasmuch as nitrogen is less inclined to form compounds in which it is quinquivalent than those in which it is trivalent. Similar remarks apply to the formation of urea from ethyl chlorocarbonate, ethyl carbonate, and the urethanes. Its formation from cyamide, $CN—NH^2$, is also very easily explained if it be supposed to consist of carbamide, being, in fact, analogous to a large number of the transformations which cyanogen-compounds undergo under the influence of water (Heintz).

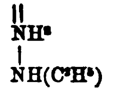
On the other hand, the identity of urea and carbamide, which seems to follow from the preceding considerations, is in discordance with the fact established by Wanklyn a. Gamgee, that urea differs from amides in general in its behaviour with alkaline permanganates, inasmuch as when oxidised by excess of potassium permanganate in alkaline solution, it gives off all its nitrogen in the free state, whereas when amides are thus treated, the nitrogen is wholly converted into nitric acid. Wanklyn a. Gamgee represent urea by the formula $C\left\{\begin{matrix}(NH)''\\ NH^2\\ OH\end{matrix}\right.$, but do not give any specific reasons for the adoption of this particular formula.

Bunte (*Ann. Ch. Pharm.* cli. 184) points out that the question about the relation of urea to carbamide might be elucidated by ascertaining the greatest number of isomeric substitution-products that can be formed by the substitution of any particular radicle, ethyl, for example, in its molecule. For in carbamide, $H^2N—CO—NH^2$, in which both atoms of nitrogen are trivalent, and all the nitrogen- and hydrogen-atoms are symmetrically disposed, the number of such possible isomeric derivatives must be less than in urea regarded as $CO=NH^2—NH^2$, in which one atom of nitrogen is quinquivalent, and the arrangement is not symmetrical. For example, carbamide can yield but one monoethylated derivative; whereas urea, if it consists of $CO=NH^2—NH^2$, may yield the two isomeric ethyl-ureas:



$$\begin{array}{l}CO\\ \parallel\\ NH(C^2H^5)\\ |\\ NH^2\end{array}$$

and



$$\begin{array}{l}CO\\ \parallel\\ NH^2\\ |\\ NH(C^2H^5)\end{array}$$

The former of these, by partial reduction to carbamic acid, would yield ethyl-carbamic acid and ammonia, whereas the latter would yield carbamic acid and ethylamine.

Preparation of Urea.—According to J. Williams (*Chem. Soc. J.* [2] vi. 63) lead cyanate is much better adapted for the preparation of urea than the potassium salt. It is merely necessary to digest equivalent quantities of this lead salt and ammonium sulphate at a moderate heat, with a sufficient quantity of water, then filter and evaporate. Compound ureas may be prepared in like manner by digesting the sulphates of the corresponding amines with cyanate of lead.

Reactions.—1. Urea heated with *carbon bisulphide* to 100° in a sealed tube, yields carbon oxysulphide and ammonium sulphocyanate:

$$CON^2H^4 + CS^2 = COS + CSN.NH^4.$$

With alcohol and carbon bisulphide the products are mercaptan, carbon dioxide, and ammonium sulphocyanate:

$$CON^2H^4 + CSS + C^2H^5OH = C^2H^5SH + CO^2 + CSN.NH^4$$

(Ladenburg, *Zeitschr. f. Chem* [2] v. 253).—2. Urea heated with *aldehyde-ammonia* and *ammonium acetate* yields aldehydine, NC^8H^{11} (p. 82):

$$4(C^2H^4O.NH^3) = NC^8H^{11} + 3NH^3 + 4H^2O$$

(Ador a. Baeyer, *ibid.* iv. 724).—3. With *glycocine* urea yields hydantoic acid (p. 702).—4. Respecting the reaction of urea with *amido-benzoic acid*, see page 318.

Compounds of Urea with Phosphoric Acid.—Lehmann (*Buchn. Repert.* xv. 224) described a crystalline compound of phosphoric acid and urea, which he obtained from pigs' urine after the animals had been fed upon pure clover. To this compound he assigned the improbable formula $CON^2H^4.2H^2O.P^2O^5 + aq.$ Schmeltzer a. Birnbaum (*Zeitschr. f. Chem.* [2] v. 206) have obtained the same compound, together with ammonium phosphate, $(NH^4)H^2PO^4$, by dissolving urea in a concentrated solution of orthophosphoric acid, evaporating in a vacuum over oil of vitriol, and recrystallising the residual mass from water. The urea phosphate forms large rhombic crystals, having the composition $CON^2H^4.H^3PO^4$. The crystals are permanent in dry air, dissolve easily in water and alcohol, sparingly in ether; heated above 100° they decompose, with brisk effervescence, into ammonia, carbon dioxide, and metaphosphoric acid:

$$CON^2H^4.H^3PO^4 = 2NH^3 + CO^2 + HPO^3.$$

The phosphoric acid in this compound is not neutralised by the urea, inasmuch as the solution does not precipitate magnesium sulphate or silver nitrate except on addition of ammonia. When evaporated with potassium or sodium carbonate, it is resolved into urea and phosphoric acid, which unites with the alkali.

Another phosphate, containing $3CON^2H^4.2H^3PO^4$, was once obtained by evaporating a mixture of phosphoric acid with excess of urea without the aid of heat. Its aqueous solution when heated yielded a crystalline precipitate of cyanuric acid, formed according to the equation $3CON^2H^4 = 3NH^3 + C^3H^3N^3O^3$. A similar decomposition of urea takes place on heating it with phosphoric anhydride (v. 950), as observed by Weltzien (*Ann. Ch. Pharm.* cvii. 219).

Substitution-derivatives of Urea.

Acetyl-urea, $CON^2H^3(C^2H^3O)$, is formed when 1 pt. of urea is heated with 2 pts. of acetic anhydride till the latter boils, the acetyl-urea then separating out on cooling.

Chloracetyl-urea, $CON^2H^3(C^2H^2ClO)$, is formed by the action of chloracetyl chloride on urea; it appears to be acted upon by potassium cyanide (Jazukowitsch, *ibid.* 234).

Amyl-ureas. (Wurtz, *Bull. Soc. Chim.* [2] vii. 141).—*Primary Amyl-urea,* $C^6H^{14}N^2O = CON^2H^3(C^5H^{11})$, formed by the action of ammonia on amyl cyanate (i. 754), crystallises in glistening needles which melt at 120°, and dissolve in 28·1 pts. of water at 27°.

Secondary Amyl-urea or *Pseudo-amylene-urea,* $CON^2H^3(C^5H^{10}H) = CON^2H^3(CH^3)(C^4H^8)$, is produced by the action of ammonia on amylene cyanate (p. 114), and may be prepared by mixing amylene hydriodide with silver cyanate at a very low temperature, then distilling, and agitating the strong-smelling distillate with excess of aqueous ammonia. Secondary amyl-urea then separates in the course of 24 hours, as a crystalline mass, which may be purified by recrystallisation from hot water. It forms beautiful needles, which melt at 151°, and then sublime partially, with evolution of ammonia; dissolves in 79·8 pts. of water at 27°, easily in alcohol. Heated with strong potash-ley to 140°–150°, it is resolved into carbon dioxide, ammonia, and isoamylamine (p. 116). In contact with nitric acid diluted with an equal volume of water, it is converted into an oily nitrate, which in contact with dry air gives off nitric acid and becomes covered with crystals; the mother-liquor yields crystals of ordinary nitrate of urea.

Secondary Diamyl-urea or *Pseudo-diamylene-urea,* $C^{11}H^{24}N^2O = CON^2H(CH^3)(C^4H^8)(C^5H^{11}) = CON^2H^2(C^5H^{10}.H)^2$, is formed, together with potassium carbonate, by heating amylene cyanate with caustic potash in a closed flask:

$$2C^5H^{10}\left\{\begin{matrix}H\\CNO\end{matrix}\right. + 2KHO = \left.\begin{matrix}CO\\K^2\end{matrix}\right\}O^2 + N^2\left\{\begin{matrix}CO\\(C^5H^{10}.H)^2.\\H^2\end{matrix}\right.$$

It sublimes in the flask in colourless needles, which may be purified by dissolving them in alcohol and mixing the solution with water till it begins to show turbidity. It is very volatile, sublimes without melting, is nearly insoluble in water, and is precipitated by water from its solution in nitric acid. It is not attacked by potash at the temperature of boiling oil.

Amylene cyanate is likewise resolved into carbonic anhydride and secondary amyl-urea, by prolonged contact with water.

Benzoyl-urea, $CON^2H^3(C^7H^5O)$, is obtained by heating equal parts of benzoic anhydride and urea to 140°–150°. The whole mass crystallises on cooling, and on treating it with alcohol, benzamide and the excess of benzoic anhydride are dissolved, while cyanuric acid and benzoyl-urea remain behind. By repeated crystallisation from ammoniacal water, the cyanuric acid may be removed and the benzoyl-urea obtained in colourless needle-shaped crystals; the quantity is, however, but small (Geuther, Schertz a. Maish, *Zeitschr. f. Chem.* [2] iv. 299).

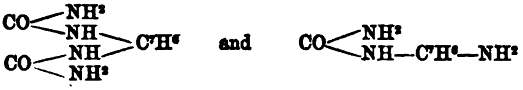
Formyl-urea, $C^2H^4N^2O^2 = CON^2H^3(CHO)$, isomeric with oxamide, is produced by heating equivalent quantities of urea and formic acid, first in the water-bath, afterwards over the open fire till gas begins to escape. The liquid on cooling solidifies to a pulp of small white crystals of formyl-urea, easily soluble in water, slightly soluble in cold, more easily in hot absolute alcohol. From the alcoholic solution it crystallises out unaltered on evaporation, but not from the aqueous solution, being resolved by the water into formic acid and urea. When boiled with potash, it gives off ammonia and yields formic acid, but not in the cold. Formyl-urea melts at 159° and decomposes at a higher temperature, giving off ammonia and hydrocyanic acid, and leaving cyanuric acid mixed with porous charcoal. At 190° an oily compound is also formed, probably formamide. At 200° the still viscid residue swells up, blackens, and leaves porous charcoal. Formyl-urea is not obtained by the action of cyanic acid vapour on formamide, the products being cyamelide and hydrocyanic acid (Geuther, Schertz a. Maish).

Hydroxyl-urea, $CON^2H^3(OH)$.—Already described (p. 725).

Oxybenzoyl-urea, $C^8H^6N^2O^3 = CON^2H^3(C^7H^4O)''$, is formed by heating oxybenzuramic acid (p. 318) to 180°–190°. The boiling ammoniacal solution gives with hydrochloric acid a precipitate insoluble in water, alcohol, and ether, crystalline when formed in small quantities, amorphous in large quantities. The barium salt of oxybenzoyl urea $(C^8H^5N^2O^3)^2Ba + 3H^2O$ is easily decomposed by the weakest acids and by ammonia. The silver salt, $C^8H^5N^2O^3Ag$, is anhydrous (Menschutkin, *Zeitschr. f. Chem.* [2] v. 53). The same compound appears to have been obtained by Griess (*ibid.* iv. 389).

Pseudo-hexylene-urea, $C^7H^{16}N^2O^2 = CON^2H^3(C^6H^{12}H)$, is obtained by heating a mixture of silver cyanate and hexylene hydriodide (from mannite) to 50°–60°, and agitating the unpleasant-smelling liquid which then passes over with aqueous ammonia. Pseudohexylene-urea then remains as a solid mass, and after repeated crystallisation from water, forms slender needles, which dissolve easily in boiling water, in alcohol and in ether, melt at 127°, and boil with partial decomposition at about 220°. Heated with strong potash-ley to 230°–250°, it decomposes, with evolution of ammonia and formation of an oily liquid, probably isohexylamine (Chydenius, *Bull. Soc. Chim.* [2] vii. 481).

Tolylene-ureas. (Strauss, *Ann. Ch. Pharm.* cxlviii. 157).—*Tolylene-diurea,* $C^9H^{12}N^4O^2 = (CON^2H^3)^2(C^7H^6)''$, is formed when 1 mol. dissolved tolylenediamine sulphate is gradually added to a solution of 2 mol. potassium cyanate cooled with ice. A small quantity of carbon-dioxide is evolved, and a white powder separates. On evaporating to dryness and exhausting the residue with alcohol, the tolylene-urea remains together with potassium cyanate, and may be obtained pure by crystallisation from boiling water. It forms micaceous crystalline scales melting at 220°. It is nearly insoluble in alcohol, and very sparingly soluble in water, even at the boiling heat, soluble in hydrochloric and in nitric acid. When dry hydrochloric acid gas is passed over this body, 2 mol. HCl are taken up, and on dissolving the product in alcohol, the solution yields a crystalline body, which appears to be a tolylene-urea isomeric with monocyanate of tolylene-diamine. These two tolylene-ureas may be represented by the following constitutional formula:



$$CO\begin{cases}NH^2\\NH\end{cases}\!\!\!\!>C^7H^6<\!\!\!\!\begin{cases}NH\\NH^2\end{cases}\!CO \quad \text{and} \quad CO\begin{cases}NH^2\\NH—C^7H^6—NH^2\end{cases}$$

UREA, SULPHURETTED. CSN^2H^4 (J. E. Reynolds, *Chem. Soc. J.* [2] vii. 1).—This compound, the sulphur-analogue of urea, is produced from ammonium sulphocyanate in the same manner as urea from ammonium cyanate. About 500 grams of well-dried ammonium sulphocyanate are heated to about 170° for about two hours in a flask placed in an oil-bath; the flask is then left to cool, and as soon as the temperature of the fused mass has sunk to 100°, it is mixed with an equal weight of water at 80°, and the solution is quickly filtered through a small plug of cotton, to remove a small quantity of a black substance which always forms in the process. The solution, after a few hours, deposits silky needles of the sulphuretted urea, which by recrystallisation from the smallest possible quantity of water may be obtained in long slender needles or in very short thick prisms belonging to the rhombic system. It melts at 149°; does not deliquesce in moderately warm air; dissolves easily in water and alcohol, sparingly in ether. The solutions froth slightly on agitation, have a neutral reaction and somewhat bitter taste, are not coloured by ferric chloride. By heating with water to 140° for several hours, the urea is reconverted into ammonium sulphocyanate, and by prolonged heating to 100° in a sealed tube with *potassium hydrate*, it yields ammonia, together with potassium sulphydrate, carbonate, and a small quantity of sulphocyanate:

$$CSN^2H^4 + 2H^2O = 2NH^3 + CO^2 + H^2S.$$

It is decomposed in the same manner by *sulphuric* and *hydrochloric acids*. By boiling with dilute *nitric acid*, the sulphur is oxidised to sulphuric acid. With *nitrous acid* and *hypochlorites* it gives off nitrogen, also when treated with a large excess of *potassium permanganate*, the sulphur being in that case oxidised to sulphuric acid. Heated on platinum foil it volatilises without residue; when heated in a tube, it melts, boils up, giving off ammonium sulphide, carbon bisulphide and ammonia (?), then blackens, and on continued heating yields a yellow oily distillate, while a white mass resembling hydromellone remains behind.

The *nitrate*, $CSN^2H^4.HNO^3$, is obtained as a crystalline precipitate on mixing a nearly saturated solution of the sulphurea with nitric acid of sp. gr. 1·25, keeping the liquid cool. On gradually adding a nearly neutral solution of auric chloride to the saturated aqueous solution till the resulting red precipitate begins to be permanent, and leaving the solution to evaporate, the *gold-salt*, $2CSN^2H^4.AuCl^3$, is obtained in nacreous monoclinic crystals. With excess of the gold solution a very unstable reddish-yellow precipitate is obtained. A nearly neutral solution of *platinic chloride* added to a slight excess of the solution of the sulphurea produces a red crystalline precipitate, appearing under the microscope as an aggregate of long prismatic feathery crystals. Reynolds assigns to this precipitate the formula $\left.\begin{matrix}(CSN^2H^3)^2\\ Cl^2\end{matrix}\right\}PtHCl$. When on the other hand the solution of the urea is added to an acid solution of platinic chloride, a brown precipitate is formed, regarded by Reynolds as $CSH^4N^2Cl^2Pt$.* When a solution of the sulphurea is heated with *silver nitrate*, the resulting precipitate redissolves, and if the hot solution containing free nitric acid be left to cool, a crystalline mass is deposited, consisting of the unstable silver-compound $(CSN^2H^4)^2Ag^2O + 4H^2O$. A neutral solution of *mercuric nitrate* added to a rather dilute solution of the sulphurea, produces, after some time, a crystalline precipitate, apparently consisting of $(CSN^2H^4)^2.3HgO + 3H^2O$.

Sulphurea heated with *silver oxide* and water, is converted into ordinary urea (Reynolds). According to Hofmann, on the other hand, it is converted, by digestion, with oxide of silver, lead, or mercury, into **dicyanodiamide** $C^2H^4N^4$:

$$2CH^4N^2S = C^2H^4N^4 + 2H^2S.$$

Dicyanodiamide melts at 20°, and forms with silver nitrate the compound $C^2H^4N^4.AgNO^3$. Its solution in hydrochloric acid yields on evaporation large tables of the hydrochloride of *dicyanodiamidine*, which, on addition of platinic chloride, deposits a platinum salt crystallising from boiling water in tufts of needles having the composition $2(C^2H^6N^4O.HCl)PtCl^4$. Dicyanodiamidine is likewise formed when sulphurea is desulphurised in presence of ammonia (Hofmann, *Deut. chem. Ges. Ber.* 1869, 600; *Zeitschr. f. Chem.* [2] vi. 158).

UREIDES or **CONDENSED UREAS** (Schiff, *Compt. rend.* lxv. 801, lxvii. 454; *Bull. Soc. Chim.* [2] ix. 323; xi. 312; *Zeitschr. f. Chem.* [2] iv. 186, 593; in detail: *Ann. Ch. Pharm.* cli. 186).—These names are applied to a series of compounds resulting from the combination of several molecules of urea with aldehyde-residues, according to the general formula,

$$xCH^4N^2O + yC^nH^{2n}O - yH^2O.$$

Diureides, $\left.\begin{matrix}CON^2H^3\\ CON^2H^3\end{matrix}\right\}C^nH^{2n}$, are produced by the action of aldehydes on aqueous or alcoholic solutions of urea. They are well crystallised compounds insoluble in water and ether, slightly soluble in alcohol. They begin to decompose at their melting points, generally yielding ammonia, cyanuric acid, and the corresponding hydramide:

$$3(CON^2H^3)^2C^nH^{2n} = 4NH^3 + 2C^3H^3N^3O^3 + N^2(C^nH^{2n})^3.$$

Triureides, $\left.\begin{matrix}CON^2H^3\\ CON^2H^2\\ CON^2H^3\end{matrix}\right\}\begin{matrix}C^nH^{2n}\\ C^nH^{2n}\end{matrix}$, are formed by the direct action of aldehydes on pulverised urea. They are distinctly crystallised compounds resembling the diureides, and decompose at high temperatures, according to the equation:

$$3\left(\left.\begin{matrix}CON^2H^3\\ CON^2H^2\\ CON^2H^3\end{matrix}\right\}\begin{matrix}C^nH^{2n}\\ C^nH^{2n}\end{matrix}\right) = 5NH^3 + 3C^3H^3N^3O^3 + 2N^2(C^nH^{2n})^3.$$

In particular cases, *e.g.* in the formation of dibenzotriureide, a higher temperature (100°–120°) must be applied; in this case also a slight excess of urea is necessary. The product must always be treated with water and with ether, to free it from adhering urea or aldehyde.

By the action of aldehydes in excess at 120°–140° on the di- and tri-ureides, the more condensed combinations are obtained, *e.g.*:

Tetrureides; $4CH^4N^2O + 3C^nH^{2n}O - 3H^2O$.
Hexureides; $6CH^4N^2O + 5C^nH^{2n}O - 5H^2O$.

These compounds are gelatinous in the moist state, and shrink together in drying;

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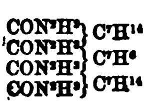
* Improbable on account of the uneven number of the atoms of H, N and Cl taken together.

they are somewhat soluble in alcohol and ether, but lose this solubility when dry. By means of œnanthol it is possible to bind together 12 molecules of urea; thus:

$$C^{89}H^{180}N^{24}O^{12} = 12CH^4N^2O + 11C^7H^{14}O - 11H^2O.$$

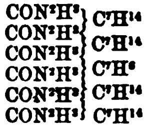
In the preparation of the more highly condensed ureas, it is possible to use aldehydes different from those which have been employed for the preparation of the di- or tri-ureides; in this manner are formed



$$\begin{array}{l} CON^2H^3 \\ CON^2H^2 \\ CON^2H^2 \\ CON^2H^3 \end{array}\begin{array}{l} C^7H^{14} \\ C^7H^6 \\ C^7H^{14} \end{array}$$

Benzodiœnantho-tetra-ureide.

and



$$\begin{array}{l} CON^2H^3 \\ CON^2H^2 \\ CON^2H^2 \\ CON^2H^2 \\ CON^2H^2 \\ CON^2H^3 \end{array}\begin{array}{l} C^7H^{14} \\ C^7H^{14} \\ C^7H^6 \\ C^7H^{14} \\ C^7H^{14} \end{array}$$

Benzotetrœnantho-hexureide.

Substitution-products of aldehydes also yield condensed ureas; nitrobenzoic aldehyde, for example, yields the corresponding diureide and tetrureide in the crystalline state. Condensed ureas are likewise formed from unsaturated aldehydes, *e.g.* acryl-diureide, $(CON^2H^3)^2(C^3H^4)''$, from acrolein.

By prolonged contact with boiling water or dilute acids, the polyureides are resolved into urea and aldehydes. Aldehydes containing hydroxyl, such as salicylic aldehyde, yield polyureides possessing alcoholic properties.

For the detailed description of the condensed ureas, see *Ann. Ch. Pharm.* cli. 186.

URIC ACID. $C^5H^4N^4O^3$.—For the purification of uric acid prepared from guano, W. Gibbs (*Sill. Am. J.* [2] xlviii. 215) dissolves the crude acid in potash, avoiding a large excess of the alkali; adds potassium dichromate (about 5 p. c. of the uric acid); boils for a short time; then dilutes the liquid with an equal volume of water, agitates it briskly with animal charcoal, and filters. On adding hydrochloric acid, the uric acid is still precipitated with a slight yellow colour. It is left to settle, separated from the liquid by decantation, and finally boiled several times with strong hydrochloric acid till it becomes perfectly white, and dissolves without colour in potash. By this method, a kilogram of uric acid having a deep yellow colour, may be rendered perfectly white in the course of an hour.

When uric acid is heated with a solution of potassium or sodium *nitrite* in presence of sulphuric acid, brisk effervescence takes place; the uric acid is completely dissolved; the liquid contains alloxan and alloxantin, and when evaporated over the water-bath, yields a considerable quantity of crystalline parabanic acid, together with a small quantity of a red flocculent substance, and a still smaller quantity of a substance which dissolves in water with bright blue fluorescence. With acetic in place of sulphuric acid, the reaction is very different; the uric acid still dissolves with effervescence as before, but the filtered solution deposits a very bulky salt, which—when potassium nitrite is used—has the composition $C^4H^2KN^5O^2$. The corresponding acid, $C^4H^3N^5O^2$, called stryphnic acid (from *στρυφνος*), on account of its bitter astringent taste, may be separated from the purified potassium salt by a mineral acid, in small yellow granular crystals soluble in hot water, and separating almost completely on cooling. It is monobasic, and its salts, excepting the lead salt, are soluble in hot water and crystallise in needles. Its formation from uric acid is represented by the equation:

$$C^5H^4N^4O^3 + HNO^2 = C^4H^3N^5O^2 + CO^2 + H^2O.$$

The quantity of stryphnic acid obtained, was, however, much less than this equation requires. The mother-liquors from which it was deposited contained allantoïn, formed according to the equation:

$$C^5H^4N^4O^3 + 2HNO^2 = C^4H^6N^4O^3 + CO^2 + N^2O^3.$$

No other fixed products were observed; the evolved gas contained nitrogen as well as carbon dioxide and nitrogen dioxide (Gibbs, *loc. cit.*).

Socoloff (*Zeitschr. f. Chem.* [2] v. 78) gives a different account of the action of nitrous acid upon uric acid. According to his experiments, the first products of the action of potassium nitrite and acetic acid upon uric acid, are urinilic acid $C^8H^7N^7O^6$ (p. 1120), and glycollic acid, $C^2H^4O^3$, together with nitrogen tetroxide and free nitrogen:

$$2C^5H^4N^4O^3 + 3HNO^2 + N^2O^3 = C^8H^7N^7O^6 + C^2H^4O^3 + 3NO^2 + 3N.$$

But the nitrogen tetroxide is immediately decomposed by the water, forming nitric and nitrous acids, by which the glycollic acid is further oxidised to oxalic acid, so that the final products are those represented by the equation:

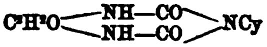
$$3C^5H^4N^4O^3 + 6HNO^3 + HNO^3 = C^6H^7N^7O^6 + 2C^2H^2O^4 + 3CO^2 + 6N^2 + 4H^2O.$$

The quantity of urinilic acid obtained is, however, less than that which corresponds to these equations, the deficiency being due to the formation of secondary products (perhaps to the reaction described by Gibbs).

Uric acid heated in a sealed tube to 160°–170° with a cold saturated solution of *hydriodic acid*, is decomposed, with formation of ammonium iodide, carbon dioxide and glycocine:

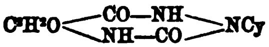
$$C^5H^4N^4O^3 + 5H^2O = 3NH^3 + 3CO^2 + C^2H^5NO^2.$$

The portion of the uric acid which appears in the form of carbon dioxide and ammonia, may be regarded as derived from 3 mol. cyanic acid or 1 mol. cyanuric acid, and in this sense uric acid may be regarded as built up from residues of glycocine and cyanuric acid, just as hippuric acid is made up of residues of glycocine and benzoic acid. Uric acid may accordingly be represented by either of the following constitutional formulæ:



$$C^3H^2O\left\langle\begin{matrix}NH—CO\\NH—CO\end{matrix}\right\rangle NCy$$

or



$$C^3H^2O\left\langle\begin{matrix}CO—NH\\NH—CO\end{matrix}\right\rangle NCy$$

(Strecker, *Zeitschr. f. Chem.* [2] iv. 215). On the structural formation of uric acid and its derivatives, see further (Strecker, *ibid.* 362).

URINILIC ACID. $C^6H^7N^7O^6$.—A tribasic acid, produced, according to Socoloff (*loc. cit.*), by the action of nitrous acid (potassium nitrite and acetic acid) on uric acid. It is slightly soluble in water, easily soluble in alkalis and alkaline carbonates, and is precipitated therefrom by hydrochloric acid, as a heavy yellow crystalline powder; from a boiling aqueous solution it separates in short thick colourless prisms. Heated with nitric acid of sp. gr. 1·30 to 1·35, it dissolves without evolution of gas, and the solution on cooling deposits small greenish, flat crystalline needles of a new acid. On further heating the nitric acid solution, red fumes are evolved, and the new acid no longer separates. Urinilic acid does not dissolve in strong sulphuric acid at ordinary temperatures.

The urinilates of the *alkali-metals* crystallise well, are very soluble in water, nearly insoluble in alcohol. Those of the *earth-metals* are white crystalline precipitates, insoluble in water and in acetic acid. Some of the salts, the copper salt for example, after drying, absorb water with great rapidity. The potassium, barium, strontium, and calcium salts are trimetallic and anhydrous. The *di-argentic salt*, $C^6H^5N^7O^6Ag^2$, is a white pulverulent precipitate, which turns brown when exposed to light or boiled with water. The *tri-argentic salt*, $C^6H^4N^7O^6Ag^3$, is precipitated from a slightly alkaline solution of the potassium salt, as a white gelatinous mass which blackens quickly, especially when heated or exposed to light. The *cadmium salt* is a white crystalline powder containing $C^6H^5N^7O^6Cd + 3H^2O$. The *cupric salt*, $C^6H^5N^7O^6Cu + 4H^2O$, is precipitated, on mixing cold dilute solutions of the potassium salt and cupric sulphate, in short slender needles, having exactly the colour of cuprous oxide; from hot solutions, in greenish-brown flakes, which are gradually converted into the red needles (Socoloff).

UROMELANIN. $C^{36}H^{43}N^7O^{10}$ (Thudichum, *J. pr. Chem.* civ. 257; *Zeitschr. f. Chem.* [2] v. 31).—A colouring matter of urine, which separates, on treating urine with sulphuric acid, as a hard, brittle, shining black mass (Preuss's peculiar black matter), insoluble in water, slightly soluble in alcohol, very soluble in the fixed alkalis and in ammonia, from which solutions it is precipitated by acids. From solution in a small quantity of ammonia it is precipitated by most soluble salts of the earth-metals and heavy metals. Silver nitrate precipitates it, after addition of acetic acid. By dry distillation it gives off white vapours condensing to a neutral oil, in which mercuric nitrate forms a red precipitate. Nitric acid dissolves uromelanin, forming a dark red solution, from which water throws down an orange-red mass. Fuming sulphuric acid dissolves uromelanin with purple-red colour, and water reprecipitates it from the recently prepared solution, but only partially, after long standing.

By the action of chlorine, a brown substance soluble in alcohol is produced, to which Thudichum assigns the formula $C^{36}H^{38}Cl^5N^7O^{10}$.

Uromelanin forms with barium, calcium, zinc, lead, and silver, a number of salts containing very variable quantities of metal; thus the barium salts contain from 7·2 to 13·75 p. c. barium, the silver salts from 13·4 to 19·77 p. c. silver. They are black, amorphous, partly gelatinous precipitates. *Mercuric nitrate* added to the acetic acid solution of uromelanin forms a red precipitate.

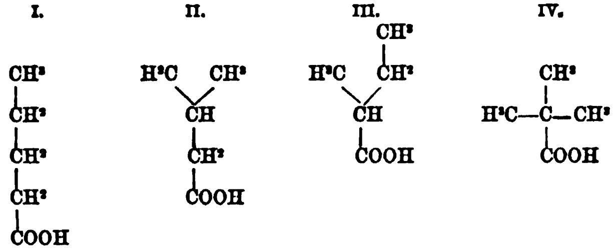
For details respecting the origin and the physiological and pathological significance of uromelanin, see the original paper.

On the colouring matters of urine, see further, *Gmelin's Handbook*, xviii. 407–413.

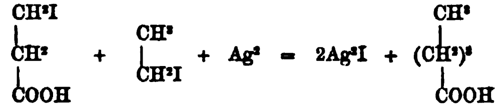
UVITIC ACID. $C^9H^8O^4$. Syn. with MESIDIC ACID (p. 821).

V

VALERIC or **VALERIANIC ACID.** $C^5H^{10}O^2 = C^4H^9.COOH$.—This acid admits of four modifications, represented by the following formulæ:



The third of these is not yet known. The first is produced by oxidation of the recently discovered normal amylic alcohol (Lieben a. Rossi, p. 106); also by the action of ethyl iodide and metallic silver on β iodopropionic acid (p. 961):



$$CH^2I.CH^2.COOH + CH^3.CH^2I + Ag^2 = 2Ag^2I + CH^3.(CH^2)^3.COOH$$

(W. v. Schneider, *Zeitschr. f. Chem.* [2] v. 343). It smells like butyric acid and boils at 185° (Lieben a. Rossi).

The second modification is the ordinary valeric acid produced by oxidation of the amyl alcohol of fermentation; and of this there are two subordinate modifications, one active to polarised light, the other inactive, produced respectively from the active and inactive modifications of amylic alcohol. The active acid boils at 170°, and turns the plane of polarisation 43° to the right in a column 50 centimetres long; the inactive acid boils at 175° (Pedler, *Chem. Soc. J.* [2] vi. 74). These modifications probably depend upon physical isomerism rather than on metamerism—in other words, they are due to difference of arrangement in the molecules of the acid, rather than in the arrangement of the atoms within the molecules.

Ordinary valeric acid is produced by reduction of angelic acid with hydriodic acid and red phosphorus (Ascher, p. 157).

The fourth modification, $C(CH^3)^3.CO^2H$, has been quite recently obtained from tertiary butylic alcohol or trimethyl-carbinol (Butlerow, *Zeitschr. f. Chem* [2] vi. 243).

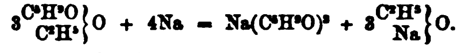
By oxidising valeric acid (the ordinary active acid) with manganese dioxide and dilute sulphuric acid, Veiel (*Ann. Ch. Pharm.* cxlviii. 160) obtained a small quantity of methyl valerate. Veiel also states, in direct contradiction to Liebig (i. 250), that when a mixture of butyric and valeric acids partly saturated with an alkali is distilled, the valeric acid passes over, and the butyric acid remains behind.

Sodium valerate in aqueous solution is slowly attacked by bromine at ordinary temperatures, more quickly when heated, very quickly in sunshine, forming carbonic acid, a small quantity of butyl bromide, and a considerable quantity of substitution-products of the latter. Nearly a third of the liquid product consists of butylene bromide (Chapman a. Smith, *Chem. Soc. J.* [2] vii. 185).

Ethyl valerate is attacked by sodium with but slight evolution of gas, yielding, according to Greiner (*Zeitschr. f. Chem.* [2] ii. 460; *Jahresb.* 1866, p. 320) a crystalline acid, $C^{20}H^{34}O^{3} = C^{5}H^{7}(C^{5}H^{9})^{2}(C^{5}H^{9}O)O^{2}$, called *divalerylene-valeric acid*, together with sodium ethylate and alcohol:

$$\underset{\text{Ethyl valerate.}}{4(C^{5}H^{9}O^{2}.C^{2}H^{5})} + 6Na = \underset{\text{Sodium divalerylene-valerate.}}{C^{20}H^{33}O^{3}Na} + \underset{\text{Sodium ethylate.}}{3C^{2}H^{5}ONa} + \underset{\text{Alcohol.}}{C^{2}H^{6}O} + Na^{2}O + H^{2}.$$

According to Wanklyn (p. 590), ethyl valerate is decomposed by sodium in the same manner as ethyl acetate, yielding sodium trivaleryl and sodium ethylate; thus



$$3\left.\begin{matrix}C^{5}H^{9}O\\C^{2}H^{5}\end{matrix}\right\}O + 4Na = Na(C^{5}H^{9}O)^{3} + 3\left.\begin{matrix}C^{2}H^{5}\\Na\end{matrix}\right\}O.$$

Greiner's divalerylene-valeric acid is probably the same as hydrogen-trivaleryl.

Isopropyl Valerate. $C^{4}H^{9}.CO^{2}CH(CH^{3})^{2}$.—See PROPYL-COMPOUNDS (p. 966).

On the estimation of valeric acid, see Zavatto a. Sestini (*Zeitschr. anal. Chem.* 1869, p. 389).

Amidovaleric Acid. $C^{5}H^{9}(NH^{2})O^{2}$. *Butyl-alanine.*—This compound, homologous with leucine (amidocaproic acid), is formed, as observed by Cahours (v. 978), by the action of ammonia on bromovaleric acid. The brominated acid is heated with strong aqueous ammonia to 100° for 24 hours; the liquid, freed from excess of ammonia, is treated with hydrated lead oxide; the filtrate, freed from lead by hydrogen sulphide, is evaporated to a syrup; and the crystalline mass which separates is washed with a mixture of alcohol and ether, and recrystallised from alcohol. It forms colourless laminæ resembling leucine, nearly opaque when dry, appearing under the microscope as very flat monoclinic prisms, easily soluble in water, nearly insoluble in cold alcohol or ether, sparingly soluble in boiling alcohol. The aqueous solution is neutral to litmus. The acid sublimes without fusion in snowy masses; when it is quickly heated, alkaline oil-drops (butylamine) collect above the sublimate. It is not decomposed by cold caustic soda. The *hydrochloride* $C^{5}H^{11}NO^{2}.HCl$ crystallises over oil of vitriol in tables permanent in the air, insoluble in ether, but easily soluble in water and in alcohol; the concentrated solution is not precipitated by platinic chloride. The *nitrate* $C^{5}H^{11}NO^{2}.HNO^{3}$ is a radio-crystalline mass, very soluble in water and alcohol, insoluble in ether, melting when heated and then detonating with evolution of red fumes. *Cupric amidovalerate*, $(C^{5}H^{10}NO^{2})^{2}Cu$, separates from a solution of the acid mixed with cupric acetate, on heating, in transparent scales slightly soluble in hot water. The *silver salt*, $C^{5}H^{10}NO^{2}Ag$, separates on adding ammonia to a hot solution of the acid mixed with silver nitrate, in spherical groups of crystals, nearly insoluble in cold, sparingly soluble in hot water, and gradually turning grey on exposure to light (Fittig a. Clark, *Ann. Ch. Pharm.* cxxxix. 199).

Bromovaleric Acid. $C^{5}H^{9}BrO^{2}$.—Fittig a. Clark (*Ann. Ch. Pharm.* cxxxix. 199) have confirmed the observation of Borodine (v. 978), that this acid cannot be distilled without decomposition. The acid prepared by heating dehydrated valeric acid with bromine to 120°-130°, and purified by passing dry air through it, decomposes at each distillation, even below 100°, yielding hydrobromic and valeric acids, together with a carbonaceous mass. According to Borodine (*Zeitschr. f. Chem.* [2] v. 342), silver valerate treated with bromine, yields Schützenberger's valerate of bromine or bromovaleric anhydride.

Chlorovaleric acid, $C^{5}H^{9}ClO$, is formed when 1 mol. sodium valerate and 1 mol. hypochlorous acid (obtained by passing chlorine through water in which levigated mercuric oxide is suspended), are brought together in a cooled vessel placed in the dark:

$$C^{5}H^{10}O^{2} + ClHO = H^{2}O + C^{5}H^{9}ClO^{2}.$$

It cannot, however, be separated by distillation from unaltered valeric acid, inasmuch as it is decomposed by heat. When a solution of sodium valerate and sodium hypochlorite is left to itself for some weeks, then acidulated with hydrochloric acid and treated with ether, the ether dissolves out chlorovaleric acid (Schlebusch, *Ann. Ch. Pharm.* cxli. 322).

VALERIC ALDEHYDE. $C^{5}H^{10}O$.—This compound heated for some time to 240° in sealed tubes, yields water, a liquid boiling between 190° and 195°, and several condensation-products boiling at higher temperatures. The compound boiling at 190°–195° has the composition $C^{10}H^{18}O$, and oxidises very readily on exposure to the air (J. Riban, *Bull. Soc. Chim.* xiii. 24).

VALERIC CHLORIDE. C^5H^9OCl.—This compound does not act in the cold, either on dry oxalic acid, or on sodium-amalgam; but when a pasty amalgam containing 2 p. c. sodium is brought in contact with a mixture of the chloride and dry oxalic acid, a reaction takes place, attended with a slight rise of temperature; and if fresh amalgam be gradually added, with continual agitation, taking care that the temperature does not rise too high, till the mass is converted into a dry powder no longer smelling of valeric chloride—water then added, and the mixture distilled, after neutralisation with sodium carbonate—an oil passes over, containing valeric aldehyde, amyl alcohol, amyl valerate, and its products of oxidation, viz. valeric aldehyde and amyl valerate, together with a peculiar oil of higher boiling point (Baeyer, *Zeitschr. f. Chem.* [2] v. 399).

VALEROLACTIC or **OXYVALERIC ACID.** $C^5H^{10}O^3 = C^4H^8(OH).COOH$. —*Ethyl-lactic acid* (iii. 463). Produced by heating bromovaleric acid with silver oxide and water. The solution filtered from silver bromide and freed from dissolved silver by hydrogen sulphide, is filtered and concentrated; the calcium salt which crystallises out is converted into a zinc salt; and the latter is decomposed by hydrogen sulphide (Fittig. a. Clark). It may also be prepared by digesting a mixture of chlorovaleric and valeric acid with excess of caustic baryta; on removing the baryta with sulphuric acid, and evaporating the filtrate, the oxyvaleric acid remains as a brownish syrup, which may be purified with animal charcoal (Schlebusch, *Ann. Ch. Pharm.* cxli. 322).

Oxyvaleric acid crystallises from a solution evaporated to a syrup over oil of vitriol in large rectangular tables, not deliquescent, easily soluble in water, alcohol, and ether; it melts at 80°, and volatilises with vapour of water, slowly also at 100° in the air-bath (Fittig a. Clark).

Most of the oxyvalerates are soluble in water. The *sodium salt*, $C^5H^9O^3Na$, forms warty crusts, easily soluble in water and in alcohol. The *barium salt*, $(C^5H^9O^3)^2Ba$, is an amorphous light yellowish mass. The *calcium salt*, $2(C^5H^9O^3)^2Ca + 3H^2O$ (or perhaps $(C^5H^9O^3)^2Ca + 2H^2O$), forms crystalline crusts more soluble in hot than in cold water. The *copper salt*, $(C^5H^9O^3)^2Ca + H^2O$, is deposited from a solution of the calcium salt mixed with cupric acetate, in light green prisms, which give off their water at 170°. The *zinc-salt*, $(C^5H^9O^3)^2Zn$, separates from a concentrated solution of the calcium salt mixed with zinc chloride, in bulky crystalline masses, slightly soluble in water, insoluble in alcohol. The *silver salt*, $C^5H^9O^3Ag$, is a bulky precipitate, which separates from hot water in feathery crystals.

VALERYLENE. C^5H^8. *Quintine* (Reboul, *Compt. rend.* lxiv. 284; *Bull. Soc. Chim.* [2] viii. 190).—This quadrivalent hydrocarbon and its bromine-compounds have been already described (v. 981). It unites slowly in the cold, easily at 100° in sealed tubes with fuming hydrochloric acid, and the product washed with alkaline water and submitted to fractional distillation, yields the mono- and dihydrochloride of valerylene, together with unaltered valerylene and a small quantity of a polymeric hydrocarbon. The *monohydrochloride*, $C^5H^8.HCl$, is a very mobile liquid insoluble in water, lighter than that liquid, and having an odour like that of amyl chloride, but stronger and more unpleasant; it boils at about 100°, that is to say, 10° higher than amylene hydrochloride. The *dihydrochloride*, $C^5H^8.H^2Cl^2$, is a liquid boiling at 150°–152°, heavier than water and insoluble therein.

Valerylene Monohydrobromide (v. 982) boils at 115°; the dihydrobromide at 180°, with slight loss of hydrobromic acid.

Fuming hydriodic acid unites directly with valerylene on agitation, forming two compounds, of which only the *monohydriodide*, $C^5H^8.HI$, has been isolated. It is a mobile liquid, sinking in water, and boiling at 140°–142°.

Acetates.—When the dihydrobromide is heated to 100° for eight hours with silver acetate suspended in ether, a product is obtained, which, when freed from silver bromide, silver acetate, and ether, contains mono- and di-acetate of valerylene:

$$\underset{\text{Dihydrobromide.}}{C^5H^8.H^2Br^2} + 2C^2H^3O^2Ag = 2AgBr + \underset{\text{Diacetate.}}{C^5H^8\left\{\begin{matrix}H^2\\(C^2H^3O^2)^2\end{matrix}\right.}$$

and

$$\underset{\text{Diacetate.}}{C^5H^8\left\{\begin{matrix}H^2\\(C^2H^3O^2)^2\end{matrix}\right.} = \underset{\text{Monacetate.}}{C^5H^8\left\{\begin{matrix}H\\C^2H^3O^2\end{matrix}\right.} + \underset{\text{Acetic acid.}}{C^2H^4O^2}.$$

Valerylene monoacetate is obtained by saturating the portion of the liquid which distils between 120° and 145° with sodium carbonate and distilling that which remains undissolved. It floats on water; is insoluble therein; has a fragrant odour like that of essence of pears, but more pungent; boils at about 153°; and is decomposed by pulverised potassium acetate, with formation of valerylene hydrate (corresponding to amylene monohydrate or secondary amyl alcohol). This latter is an aromatic liquid lighter than water, insoluble therein, boiling at 115°–120°. Sodium dissolves in it, with evolution of hydrogen, forming a solid compound, which is decomposed by water, with reproduction of the monohydrate. *Valerylene diacetate*, $C^5H^8.H^2.(C^2H^3O^2)^2$, is a somewhat thickish liquid, insoluble in water, boiling at about 205°. It is decomposed by potash, yielding acetic acid and probably valerylene-dihydrate.

Polymerides of Valerylene are formed by the action of sulphuric acid on valerylene. When the hydrocarbon is gradually mixed with strong sulphuric acid in a cooled vessel, a dark violet-red layer separates, which, by washing with water and alkali, is converted into a rather viscid yellow oil. The acid separated therefrom and neutralised with barium carbonate, yields only a small quantity of a hygroscopic salt. The yellow oil yields by fractional distillation:—1. *Divalerylene hydrate*, $2C^5H^8.H^2O$, a mobile liquid lighter than water, insoluble therein, boiling at 175°–177°, and having a strong odour like that of peppermint oil and of turpentine oil. This compound is perhaps the ether of the above-mentioned valerylene monohydrate.—2. *Trivalerylene*, $C^{15}H^{24}$, a yellow oily liquid distilling between 265° and 275°, having a sp. gr. of 0·862 at 15°, smelling like turpentine oil, with which indeed (like valerylene itself) it is polymeric.

Still higher polymerides of valerylene are contained in the increasingly viscid portion of the product of the action of sulphuric acid on valerylene, which boils above 280° and towards 350°, and in the brown-yellow mass which separates on cooling. Sulphuric acid diluted with one-third of its volume of water, acts on valerylene in the same manner as the concentrated acid, but less energetically; if the acid is diluted with half its weight, or nearly an equal volume, of water, the entire quantity of valerylene may be treated with it at once, since the mixture does not become hot till after frequent agitation. In proportion as the acid is more dilute, the product becomes richer in the ether, $2C^5H^8.H^2O$, and in trivalerylene. Zinc chloride at 160°–180° produces on valerylene the same transformations as sulphuric acid (Reboul, *Compt. rend.* lxiv. 419; *Bull. Soc. Chim.* [2] viii. 190).

VANADIUM. *Atomic Weight*, 51·3 (Roscoe, *Phil. Trans.* 1869, p. 679; 1870, p. 317; *Proc. Roy. Soc.* xviii. 37, 316; *Chem. Soc. J.* [2] viii. 344; ix. 23).

Metallic Vanadium. The only method by which this metal can be obtained in the pure state is by the reduction of a vanadium chloride (free from oxygen) in hydrogen gas. Roscoe has obtained it by heating the pure dichloride to redness for 40 to 80 hours in a stream of perfectly pure and dry hydrogen. The process is extremely difficult, owing to the avidity with which the reduced metal absorbs oxygen at a red heat, rendering it necessary to exclude every trace of air and moisture during the reduction. The chloride to be reduced is placed in a platinum boat within a porcelain tube, as the metal acts violently on glass and porcelain, and tubes of platinum are porous at a red heat.*

Metallic vanadium thus prepared appears under the microscope as a shining crystalline mass, having a strong silver-white lustre. It does not oxidise or even tarnish in the air at ordinary temperatures, or even at 100°; does not decompose water at 100°; and may be moistened with water and dried in a vacuum without gaining weight. It does not melt or volatilise at a bright red heat in hydrogen. The powdered metal thrown into a flame burns with the most brilliant scintillations. Heated quickly in oxygen, it burns vividly, forming the pentoxide; but when slowly ignited in air, it first glows and forms a brown oxide (possibly V^2O), then again absorbs oxygen and is converted into black trioxide and blue tetroxide, till at last it attains its maximum degree of oxidation. It is not soluble in *hydrochloric acid*, either hot or cold; strong *sulphuric acid* dissolves it on heating, forming a yellow solution; *hydrofluoric acid* dissolves it slowly with evolution of hydrogen; *nitric acid* of all strengths acts violently on it, evolving red fumes and forming a blue solution. Fused with *sodium hydrate*, the metal dissolves, with evolution of hydrogen and formation of a sodium vanadate. In a current of *chlorine*, the metal takes fire, and

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* For a description and figure of the apparatus used, see the paper above cited in the *Philosophical Transactions* or the *Journal of the Chemical Society*.

In the decomposition of carbothialdine, aldehyde is always reproduced. The homologous compound, *diamylidenammonium sulphocarbamate*, $CS\left\{\begin{matrix}NH^2\\SN(C^5H^{10})^2\end{matrix}\right.$, is obtained by agitating ammonium sulphocarbamate with valeral in alcoholic solution, and pouring the filtered liquid into water, as a colourless flocculent precipitate, which after washing with water, pressing between paper, and drying in a vacuum, forms a shining crystalline mass. Heated with ferric chloride it gives the sulphocyanogen reaction. *Diallylidenammonium sulphocarbamate*, $CS\left\{\begin{matrix}NH^2\\SN(C^3H^4)^2\end{matrix}\right.$, obtained by agitating acrolein with ammonium sulphocarbamate in aqueous solution in a cooled vessel, is colourless, apparently amorphous, insoluble in water and alcohol; gives the sulphocyanogen reaction when heated with ferric chloride (Mulder a. Bettinck).

Ethyl sulphocarbamate, $CS\left\{\begin{matrix}NH^2\\SC^2H^5\end{matrix}\right.$, is formed by the action of hydrogen sulphide on ethyl sulphocyanate. It is converted by the fixed alkalis into ethyl sulphide and metallic sulphocyanate; by ammonia into ethyl sulphide and sulphocarbamide, isomeric with ammonium sulphocyanate. A mixture of ethyl sulphocarbamate and ethyl iodide solidifies to a crystalline mass, apparently consisting of a compound of the two in equivalent proportions. The iodides of methyl and amyl, as well as the bromides of the same radicles, react in the same manner with the sulphocarbamates of ethyl and its homologues (Jeanjean, *Jahresb.* 1866, p. 501).

Ethyl-sulphocarbamic Acid. $C^3H^7NS^2 = CS\left\{\begin{matrix}NH(C^2H^5)\\SH\end{matrix}\right.$.—An alcoholic solution of ethylamine mixed with carbon bisulphide becomes hot, loses its alkaline reaction, and, if sufficiently concentrated, deposits six-sided tables of ethylsulphocarbamate of ethyl-ammonium:

$$2N(C^2H^5)H^2 + CS^2 = CS\left\{\begin{matrix}NH(C^2H^5)\\SN(C^2H^5)H^3\end{matrix}\right..$$

This salt melts at 103°, and partly sublimes without decomposition when gently heated. It is soluble in water and easily soluble in alcohol. With caustic soda it gives off ethylamine, and is converted into sodium ethylsulphocarbamate, which, on addition of hydrochloric acid, yields ethylsulphocarbamic acid in oily drops floating on the surface, and solidifying after a while to fatty crystals, On adding more hydrochloric acid, the oily drops dissolve, with evolution of carbon bisulphide, and nothing but ethylamine hydrochloride remains in solution. Ethyl-ammonium ethylsulphocarbamate is decomposed when heated to 100°, and more easily when its alcoholic solution is heated under pressure to 110°–120°, giving off hydrogen sulphide, and leaving diethylsulphocarbimide, in the form of an oily liquid, which soon solidifies to crystals:

$$CS\left\{\begin{matrix}NH(C^2H^5)\\SNH^3(C^2H^5)\end{matrix}\right. = H^2S + N^2\left\{\begin{matrix}(C^2H^5)^2\\CS\\H^2\end{matrix}\right..$$

Ethylsulphocarbamic acid in the free state resolves itself into its components, ethylamine and carbon bisulphide; but its metallic salts, especially in presence of excess of another metallic salt (*e.g.* silver nitrate or mercuric chloride), are easily resolved into ethyl-sulphocarbamide and a metallic sulphydrate (p. 1050):

$$CS\left\{\begin{matrix}NH(C^2H^5)\\SM\end{matrix}\right. = N\left\{\begin{matrix}CS\\C^2H^5\end{matrix}\right. + HMS.$$

The corresponding *methyl-* and *amyl-*compounds are obtained by similar processes, and exhibit similar reactions (Hofmann, *Zeitschr. f. Chem.* [2] iv. 686; *Jahresb.* 1868, p. 653).

Ethylic Ethyl-oxysulphocarbamate, Ethyl-xanthamide, or *Semi-sulphuretted Ethyl-urethane,* $CS\left\{\begin{matrix}NH(C^2H^5)\\OC^2H^5\end{matrix}\right.$, is produced by direct combination of ethyl-sulphocarbimide, $N(CS)(C^2H^5)$, and ethyl-alcohol, $HO(C^2H^5)$, when the two are heated together to 110° in a sealed tube for several hours, and is precipitated on mixing the resulting liquid with water, as an oil having a somewhat unpleasant alliaceous odour, and boiling, after purification, at 204°–208°. Under the influence of water, and especially in presence of acids or alkalis, it is resolved into alcohol, carbon dioxide, hydrogen sulphide, and ethylamine. With strong sulphuric acid, carbon oxysulphide is formed instead of carbon dioxide and hydrogen sulphide. The above-described compound is likewise produced by the action of alcoholic soda-solution on ethyl-sulphocarbimide; but the corresponding sodium salt is always produced at the same time by the action of the sodium hydrate, and ultimately part the vapour of the oxytrichloride (v. 992), mixed with excess of chlorine, is passed several times over a column of red-hot charcoal; the whole of the oxygen may thus be removed and ultimately perfectly pure tetrachloride obtained. The tetrachloride prepared by the first method may be purified by distillation in a current of chlorine, and afterwards in a current of carbon dioxide. The pure tetrachloride is a dark brown liquid having a sp. gr. of 1·8584 at 0°, boiling at 154°, and not solidifying at −18°. Neither at this nor at any higher temperature is it altered in its properties by treatment with chlorine. It is resolved quickly on boiling, slowly at ordinary temperatures, into the trichloride and free chlorine. When thrown into water, it immediately decomposes, forming a blue solution, identical in colour with that which is obtained by the reducing action of sulphurous or sulphydric acid on a solution of vanadic acid, and containing a vanadous salt derived from the tetroxide, V^2O^4. The solution treated with permanganate is oxidised according to the equation:

$$2VCl^4 + O + 4H^2O = 8HCl + V^2O^5.$$

The aqueous solution of the tetrachloride does not bleach; but if the vapour be passed into water, a liquid is obtained which bleaches litmus. Vanadium tetrachloride acts violently on alcohol and ether, forming deep-coloured liquids.

When bromine and vanadium tetrachloride are heated together in a sealed tube, no combination takes place, but trichloride is deposited: hence it appears that vanadium does not readily form pentad compounds with the chlorous elements.

Iodine does not attack either trioxide or nitride of vanadium at a red heat.

Vanadium Mononitride, VN, has been already described (v. 987) as obtained by the action of ammonia on vanadyl trichloride. A more economical method is to subject ammonium metavanadate, NH^4VO^3, at a white heat to a current of dry ammonia; the pure mononitride then remains behind. It may also be prepared by heating the trioxide or the dichloride to whiteness in a platinum tube through which dry ammonia gas is passed.

Metallic Vanadates. The analogy between the vanadates and phosphates has been already pointed out (v. 989). The vanadates examined by Berzelius and v. Hauer, were chiefly metavanadates, $M'VO^3$, or $M''V^2O^6$, and anhydrovanadates, $2MVO^3.V^2O^5$, or $M''V^2O^6.V^2O^5$. Roscoe has lately obtained several orthovanadates, M^3VO^4, and tetrabasic vanadates, or pyrovanadates, $M^4V^2O^7$.

The soluble vanadates of these three classes exhibit, at ordinary temperatures, an order of stability which is the reverse of that of the corresponding phosphates, the metavanadates being the most and the orthovanadates the least stable. Thus sodium orthovanadate, Na^3VO^4, splits up in solution into caustic soda and the pyrovanadate; and the soluble pyrovanadates in aqueous solution are easily decomposed by carbonic acid into an alkaline carbonate and a monobasic or metavanadate. At high temperatures, on the other hand, the tribasic salts are the most stable; thus vanadium pentoxide, when fused with sodium carbonate, eliminates 3 mol. CO^2, and forms an orthovanadate, but when boiled with a solution of sodium carbonate it forms a metavanadate. Hence, as most of the native vanadates are tribasic, we may assume that they have been formed at high temperatures.

The soluble orthovanadates form with *ferric salts* a light brownish-yellow gelatinous precipitate, soluble in hydrochloric, insoluble in acetic acid; with *ferrous salts*, a dark grey precipitate; with *manganous salts*, brownish-yellow crystalline; with *zinc salts*, white gelatinous; with *cobalt salts*, brown-grey gelatinous; with *nickel salts*, canary-yellow crystalline; with *copper salts*, apple-green; with *mercuric salts*, orange-yellow; and with *aluminium salts*, a bright yellow gelatinous precipitate, soluble in excess of either reagent, the solution thus formed yielding a white precipitate on boiling.

Sodium Salts.—The *tri-sodic salt* or *sodium orthovanadate*, $Na^3VO^4 + 16H^2O$, remains as a white crystalline mass when a mixture of 3 mol. sodium carbonate and 1 mol. vanadium pentoxide is fused till no more carbon dioxide is evolved. This mass dissolves easily in water, and on addition of absolute alcohol two layers of liquid are formed, the lower of which solidifies after a while to a mass of needle-shaped crystals having the composition above given. In analysing this and the following salt, the vanadic acid was precipitated in the form of the perfectly insoluble orthovanadate of lead (p. 1127); this was dried at 100° and weighed, then dissolved in nitric acid and decomposed by sulphuric acid, and the solution of vanadium pentoxide in excess of this acid gave on evaporation a finely crystalline mass. The filtrate from the lead precipitate yielded sodium sulphate on evaporation.

Tetrasodic Vanadate or *Sodium Pyrovanadate.* $Na^4V^2O^7 + 18H^2O$.—The trisodic salt, when repeatedly crystallised, splits up into the tetrasodic salt and caustic soda:

$$2Na^3VO^4 + H^2O = Na^4V^2O^7 + 2NaHO.$$

The tetrasodic salt crystallises in beautiful six-sided tables, easily soluble in water, insoluble in alcohol, and is precipitated by the latter liquid from aqueous solution in white scales having a silky lustre. As long as it contains free alkali or trisodic salt, it forms, on precipitation with alcohol, oily drops which gradually solidify.

The tetrasodic salt is always formed in the first instance when vanadium pentoxide is fused with excess of sodium carbonate, and can be easily obtained in the pure state by recrystallisation.

The corresponding *calcium* and *barium vanadates*, $Ca^2V^2O^7$, and $Ba^2V^2O^7$, are white precipitates obtained by adding the chlorides to a solution of tetrasodic vanadate. The calcium salt contains 2½ mol. water; the barium salt is anhydrous. When calcium chloride is added to a solution of the trisodic salt, dicalcic vanadate is precipitated, and the solution contains calcic hydrate.

Lead Salts.—The *triplumbic vanadate*, or *Orthovanadate*, $Pb^3(VO^4)^2$, is obtained as a light yellow insoluble powder on precipitating trisodic vanadate with a soluble lead salt. The *orthovanadato-chloride*, $3Pb^3(VO^4)^2.PbCl^2$, which occurs native as *vanadinite*, may be artificially prepared by melting for five hours a mixture of vanadium pentoxide, lead oxide, and lead chloride in the required proportions, with an excess of sodium chloride. After cooling, a greyish crystalline mass is left, containing cavities filled with long crystals having the same colour as the mass, and distinguishable under the microscope as six-sided prisms. The crystalline powder, after being freed by boiling from soluble chloride, exhibits the composition of native vanadinite; its sp. gr. at 12° is 6·707, that of the natural mineral 6·886. *Basic diplumbic Vanadate*, $2Pb^2V^2O^7.PbO$, is precipitated as a pale yellow powder when lead acetate is added to a solution of tetrasodic vanadate, the liquid acquiring an acid reaction. It is quite insoluble in water and in dilute acetic acid, but dissolves readily in nitric acid.

Silver Vanadates.—The *orthovanadate*, Ag^3VO^4, is obtained as an orange-coloured precipitate on adding silver nitrate to a recently prepared and perfectly neutral solution of trisodic vanadate. It is insoluble in water, but dissolves readily in ammonia and in nitric acid. The *pyrovanadate*, $Ag^4P^2O^7$, separates on adding a neutral solution of silver nitrate to the corresponding sodium-salt, as a yellow, dense, crystalline precipitate, resembling in colour the ordinary phosphate of silver.

VAPOUR-DENSITY. A new method of determining vapour-densities, founded on the well-known method of Gay-Lussac, is described by A. W. Hofmann (*Deut. chem. Ges. Ber.* 1868, i. 198). A graduated glass tube about a metre long and 15 to 20 mm. wide, is filled with mercury and inverted in a mercury trough, whereby a barometric vacuum, 20 to 30 mm. high, is formed at the top. This part of the tube is enclosed in another tube 30 to 40 mm. wide and 80 to 90 mm. long, drawn out at the top to a conducting tube of moderate width, which is bent at right angles, and connected with a glass or copper vessel in which water, aniline, or other liquid can be boiled. The outer tube is closed at bottom with a cork having two apertures, one to admit the barometer-tube, the other for an escape-tube. By this arrangement, a stream of vapour of water, aniline, or other volatile liquid can be made to pass through the space between the two tubes, so as to keep the upper part of the barometer-tube at the temperature required for the determination. The substance whose vapour-density is to be determined, is introduced into the barometric vacuum in small glass tubes fitted with ground stoppers, which are forced out by the tension of the vapour. The great advantage of this method is that, under the very small pressure to which the enclosed vapour is subjected—which may be reduced to 20 or even 10 millimetres of mercury—the determinations may be made at comparatively low temperatures. Thus, in the case of liquids boiling under the ordinary pressure at 120° or even 150°, the vapour-density may be accurately determined at the temperature of boiling water. For the working details and a figure of the apparatus, we must refer to the original paper.

VIRIDIC ACID. This acid, obtained by Rochleder from caffetannic acid, may also be prepared directly from coffee-berries, by boiling them with ether-alcohol to remove the fat, and exposing them in the form of moist powder to the air. The powder turns green in a few days, and if then exhausted with acetic acid and alcohol, yields viridic acid as a brown amorphous mass (C. O. Čech, *Ann. Ch. Pharm.* cxliii. 366).

VOLTAITE. This mineral has been found, in non-cleavable octohedrons with cubic and dodecahedral faces, mixed with ferrous sulphate, in an iron mine at Kremnitz. Colour, black to violet; hardness, 3; sp. gr. 2·79. Analysis gave 48·0 p. c. SO^3, 5·1 Al^2O^3, 12·9 Fe^2O^3, 15·6 FeO, 3·6 K^2O, and 15·3 H^2O (Tschermak, *Wien. Akad. Ber.* lvi. [1] 824).

W

WALNUT. See Juglans (p. 763).

WATER. On the electrolysis of water in contact with silver, see Rundspaden, (*Ann. Ch. Pharm.* cli. 306; *Zeitschr. f. Chem.* [2] vi. 49).

On the influence of water on double decompositions, and on the accompanying thermic effects, see Marignac (*Compt. rend.* lxix. 1180; *Zeitschr. f. Chem.* [2] vi. 69).

WAX from STRAW. The straw of cereals yields a white wax, greasy to the touch, insoluble in water and in caustic alkalis, soluble in alcohol, especially when warm, also in ether and in carbon bisulphide, and crystallising from alcoholic solution by slow cooling in small tables or shining nacreous scales. At 42° it melts to a colourless oil, which makes grease spots on paper, and solidifies on cooling to a hard brittle mass. It boils at about 300°, almost without residue; the portion distilling over between 300° and 303° melts as before at 42°. The wax is easily attacked by bromine at a gentle heat. Nitric acid, even when hot and concentrated, attacks it with difficulty, forming a compound soluble in caustic alkalis. Strong sulphuric acid attacks the wax when heated, forming a solution from which water throws down a flocculent precipitate probably consisting of the original compound (Radziszewski, *Deut. chem. Ges. Ber.* ii. 207).

WOOL. On the composition of raw sheep's wool, see Märcker a. Schulze (*J. pr. Chem.* cviii. 193; *Zeitschr. f. Chem.* [2] vii. 281).

X

XANTHINE. $C^5H^4N^4O^2$. Neubauer's method of estimating xanthine and separating it from sarcine in muscular flesh, is given under Sarcine (p. 1013); see further *Zeitschr. f. Chem.* [2] v. 31.

XENOL. Syst. with Xylenol.

XONALTITE. A hydrated calcium silicate, found at Tetela de Xonatla in Mexico. It occurs intergrown with apophyllite and bustamite, forming white or bluish-grey concentric layers. Fine-grained or compact; very hard and tough; sp. gr. 2·710 to 2·718. Analysis gave for the white variety, A, and the grey variety, B, the following numbers:

SiO^2	CaO	MgO	MnO	FeO	H^2O		
49·58	43·56	—	1·79	1·31	3·70	=	99·94
50·25	43·92	0·19	2·28		4·07	=	100·71

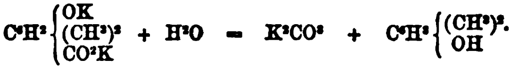
agreeing nearly with the formula $4CaSiO^3 + H^2O$ (Rammelsberg, *Jahrb. Min.* 1866, p. 718).

XYLENEDIAMINE. Syn. with Xylylenediamine (p. 1132).

XYLENOL. $C^8H^{10}O = C^6H^3(CH^3)^2OH$.—*Dimethyl-phenol*, *Xenol*, *Xylylic phenol* (Wroblevsky, *Zeitschr. f. Chem.* [2] iv. 232; *Bull. Soc. Chim.* [2] x. 286; Wurtz, *Jahresb.* 1868, p. 459).—Prepared by fusing the potassium salt of xylyl-sulphurous acid, $C^8H^9SO^3K$, with twice its weight of potassium hydrate, decomposing the resulting mass with hydrochloric acid, and distilling in a current of steam, or digesting with ether, which dissolves out the xylenol. According to Wroblevsky, it is a liquid boiling at 214·2° (corr.), having a sp. gr. of 1·0233 at 22°, and smelling like phenol; slightly soluble in water; coloured faintly greenish by ferric chloride. By treatment with sodium and carbon dioxide, it is converted into xyletic acid, $C^9H^{10}O^3$ (Wroblevsky).

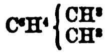
Wurtz, by decomposing the fused alkaline mass obtained, as above, with hydrochloric acid, digesting it with ether, and distilling, obtained a liquid which passed over at 210°, and when exposed to a winter temperature, separated into two isomeric modifications, one crystalline, the other liquid.—α. *Solid xylenol* dissolves abundantly in alcohol and ether; melts at 75° to a liquid which has a sp. gr. of 0·709 at 81°, and contracts considerably in solidifying; it boils at 213·5°, and when heated above its melting point gives off copious fumes which condense on the cooler parts of the vessel.—β. *Liquid xylenol* is colourless and strongly refractive; has a sp. gr. of 1·036 at 0°, and 0·9760 at 81° (expansion-coefficient 0·000868); boils at 211·5° (bar. at 759·7 mm.); mixes in all proportions with alcohol and ether; is slightly soluble in water, and itself dissolves small quantities of that liquid.

Solid xylenol is also produced by heating the neutral potassium salt of oxymesitylenic acid with excess of potash, just as phenol is obtained from potassium salicylate:



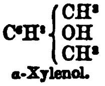
$$C^6H^2\begin{cases}OK\\(CH^3)^2\\CO^2K\end{cases} + H^2O = K^2CO^3 + C^6H^3\begin{cases}(CH^3)^2\\OH\end{cases}.$$

The xylenol thus prepared agrees almost exactly in its physical properties with that obtained by Wurtz (melts at 73° and boils at 216°). Now as mesitylenic acid, when heated with lime, yields metaxylene (p. 293), in which the two methyl-atoms occupy the places 1, 3, it follows that in the phenol obtained from oxymesitylenic acid, the two methyl-atoms will also occupy a similar position, having the hydrogen-atom between them. The isomerism of solid (α) and liquid (β) xylenol may accordingly be represented as follows:



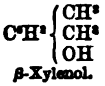
$$C^6H^4\begin{cases}CH^3\\CH^3\end{cases}$$

Xylene (1, 3).



$$C^6H^3\begin{cases}CH^3\\OH\\CH^3\end{cases}$$

α-Xylenol.



$$C^6H^3\begin{cases}CH^3\\CH^3\\OH\end{cases}$$

β-Xylenol.

Bromine converts xylenol into tribromoxylenol, $C^8H^7Br^3O$, which forms golden-yellow shining crystals, melting at 141° (Wroblevsky).

When α-xylenol suspended in water and cooled is treated with bromine, and the excess of bromine evaporated, dibromoxylenol ,$C^8H^8Br^2O$, remains as a laminar mass, which crystallises from alcohol in large golden-yellow plates, melting at 176°, and subliming at higher temperatures in delicate golden-yellow spangles. It is easily soluble in hot, less easily in cold alcohol, insoluble in water and in sodium carbonate; dissolves in alkalis, especially when warmed, but apparently not without decomposition (Fittig a. Hoogewerf, *Zeitschr. f. Chem.* [2] v. 170).

Xylenol is isomeric with Müller's xylylic phenol, with phlorol, and with the so-called toluylic alcohol, $C^6H^4\begin{cases}CH^3\\CH^2OH\end{cases}$, better called xylylic alcohol (v. 1062).

XYLETIC ACID, $C^9H^{10}O^3 = C^8H^9O.CO^2H$, isomeric with phloretic, tropic, and melilotic acids, is produced by treating xylenol with sodium and carbon dioxide. When separated from the resulting sodium salt by hydrochloric acid, and freed from admixed xylenol by a current of steam, it forms white crystals, melting at 155°, and sublimable. It is more soluble in hot than in cold water; colours ferric chloride violet. The *barium salt*, $(C^9H^9O^3)^2Ba + H^2O$, and the *calcium salt*, $(C^9H^9O^3)^2Ca + 2H^2O$, form needle-shaped crystals, which give off their water at 150° (Wroblevsky, *loc. cit.*).

XYLIC or XYLYLIC ACID. $C^9H^{10}O^2 = C^6H^3(CH^3)^2.CO^2H$. Two modifications of this acid, distinguished as *xylic* and *paraxylic*, are formed, together with xylidic acid, $C^6H^3(CH^3).(CO^2H)^2$, by oxidising pseudocumene (prepared by methylisation of metaxylene, p. 296) with dilute nitric acid (1 vol. acid of sp. gr. 1·4 and 2 vol. water) at the boiling heat. At the end of the reaction, a crystalline mass separates; and on repeatedly boiling this mass with water, xylic and paraxylic acids pass over, while xylidic acid and nitro-acids remain behind. The distillates are supersaturated with sodium carbonate and boiled down (whereupon admixed nitropseudocumene passes over) and the concentrated solution is supersaturated with hydrochloric acid. The mixture of acids thereby separated is finally treated with tin and hydrochloric acid, to remove the nitro-compounds, and converted into calcium salts, which may be separated by their different solubility in water, the xylate being more soluble than the paraxylate.

Xylic acid crystallises from alcohol in colourless monoclinic prisms, melting at 120°. It also melts in boiling water, then dissolves, and crystallises for the most part in needles on cooling. In alcohol it is much more soluble, especially at the boiling heat.

Calcium xylate, $(C^9H^9O^2)^2Ca + 2H^2O$, crystallises in hard, transparent, colourless, monoclinic prisms, which dissolve abundantly, though slowly, in water. The *barium salt*, $(C^9H^9O^2)^2Ba + 8H^2O$(?), is very soluble in water, and remains on evaporation as a radio-crystalline mass.

By potassium chromate and dilute sulphuric acid, it is easily and completely oxidised to carbonic and acetic acids, a small quantity of xylidic acid being sometimes also formed as a secondary product.

Paraxylic acid crystallises from alcohol in rather large concentrically grouped, colourless, pointed prisms, melting at 163°. It is nearly insoluble in cold, very sparingly in boiling water, does not melt when boiled with water, dissolves very easily in alcohol. When oxidised with nitric acid, it yields xylidic acid identical with that which is obtained by oxidation of xylic acid. *Calcium paraxylate*, $(C^9H^9O^2)^2Ca + 3\frac{1}{2}H^2O$, crystallises in soft white spiculæ, often grouped in tufts, dissolving quickly when warmed with water. The *barium salt*, $(C^9H^9O^2)^2Ba + 4H^2O$, crystallises in tufts or stellate groups of hard colourless needles. It is more soluble in water than the calcium salt, but less soluble than barium xylate (Fittig a. Laubinger, *Zeitschr. f. Chem.* [2] iv. 597).

In pseudocumene, $C^6H^3(CH^3)^3$ (p. 296), as shown by Bieber a. Fittig (*ibid.* v. 434), the three methyl-atoms occupy the relative positions denoted by 1, 3, 4. Now, as this hydrocarbon, when oxidised with nitric acid, yields simultaneously the two isomeric acids xylic and paraxylic, it follows that two of its methyl-atoms are oxidised with equal facility to CO^2H. The positions of these two equally oxidable methyl-atoms may be determined by removing the carboxyl-groups from the two acids, and observing what modifications of xylene or dimethyl-benzene. $C^6H^4(CH^3)^2$, are thereby produced. Now it is found that xylic acid, when heated with lime, yields metaxylene or isoxylene (1, 3), and paraxylic acid similarly treated yields orthoxylene (3, 4); hence it appears that in the formation of xylic acid from pseudocumene, the methyl-atom occupying the position 4, is oxidised to carboxyl, and in the formation of paraxylic acid, the methyl-atom occupying the position 1, undergoes that change: thus;

		1	2	3	4	5	6
Benzene . . .	C^6	H	H	H	H	H	H
Pseudocumene .	C^6	(CH^3)	H	(CH^3)	(CH^3)	H	H
Xylic acid . .	C^6	(CH^3)	H	(CH^3)	$(CO^2H$	H	H
Paraxylic acid .	C^6	(CO^2H)	H	(CH^3)	(CH^3)	H	H

Identical with the xylic acid above described is that which Schaper obtained by oxidising cumene (prepared by dry distillation of calcium cumene-sulphate) with dilute nitric acid: melting point 125° (*Zeitschr. f. Chem.* [2] v. 545); and probably also the acid melting at 122°, which Kekulé obtained by the action of carbon dioxide and sodium on bromoxylene. The xylic acid described by Hirzel a. Beilstein, as melting at 204°, and as yielding insolinic acid by further oxidation, and the liquid xylic acid described by Kügler a. Beilstein, both produced by oxidation of cumene (v. 1062) seem to require further investigation.

XYLIDIC ACID. $C^9H^8O^4 = C^6H^3\begin{cases}CH^3\\CO^2H\\CO^2H\end{cases}$.—This bibasic acid, isomeric with uvitic or mesidic acid, is formed, as above stated, by the oxidation of xylic or paraxylic acid, or directly from pseudo-cumene, by simultaneous oxidation of the methyl-atoms 1 and 4, in the same molecule of the hydrocarbon. It is a white, amorphous, bulky mass, nearly insoluble in cold water, very slightly soluble in boiling water, easily in alcohol, especially when warm, and crystallises therefrom, by spontaneous evaporation, in white granulo-crystalline nodules. It melts at 280°–283°, and sublimes easily (especially in a stream of dry carbon dioxide), in hard colourless needles melting at 291°. *Calcium xylidate*, $C^9H^6O^4Ca$, forms indistinct white scales, very soluble in water, and containing water of crystallisation, which they give off over oil of vitriol. The *barium salt*, $C^9H^6O^4Ba$, remains on evaporation as a radio-crystalline mass, more soluble in water than the calcium salt, precipitated from the concentrated solution by alcohol, in colourless flocks. The *silver salt* is obtained as a white flocculent pre-

The phenyl-compound was obtained some years ago by Hofmann, and the naphthyl-compound by Hall (v. 521); and Hofmann has recently, by the reaction above mentioned, obtained other sulphocarbimides belonging to the fatty as well as to the aromatic group. The sulphocarbimides are distinguished from the normal sulphocyanic ethers by their intensely pungent odour, and by their capability of uniting directly with ammonia and with monamines, giving rise to alcoholic derivatives of sulphocarbamide. In these respects they resemble volatile oil of mustard, which is in fact allylic sulphocarbimide, $N(CS)(C^3H^5)$, and may be regarded as the type of the group. Hofmann, indeed, designates these bodies by the generic name of *Mustard-oils* (*Senföle*). It is remarkable, however, that allylic sulphocarbimide, and not normal allylic sulphocyanate (which is not known), is produced by distilling potassium sulphocyanate with allyl iodide.

Ethyl-sulphocarbimide or **Ethylic Isosulphocyanate**, $N(CS)(C^2H^5)$, is produced by distilling diethyl-sulphocarbamide with phosphoric anhydride or anhydrous hydrochloric acid, but is more easily prepared by the following process, depending on the decomposition of metallic ethyl-sulphocarbamates; thus:

$$\underset{\substack{\text{Ethyl-sulpho-}\\\text{carbamate.}}}{CS\left\{\begin{matrix}N(C^2H^5)H\\SM\end{matrix}\right.} \quad = \quad \underset{\substack{\text{Ethyl-sulpho-}\\\text{carbimide.}}}{N\left\{\begin{matrix}CS\\C^2H^5\end{matrix}\right.} \quad + \quad \underset{\text{Sulphydrate.}}{S\left\{\begin{matrix}H\\M\end{matrix}\right.}$$

When a solution of ethyl-sulphocarbamate of ethylamine (produced by direct combination of ethylamine with carbon bisulphide, p. 1049), is mixed with silver nitrate, a white precipitate of silver ethyl-sulphocarbamate is produced, which blackens even at ordinary temperatures, and more quickly when heated, with formation of silver sulphydrate and ethyl-sulphocarbimide, which latter passes over abundantly with the vapour of water on boiling, hydrogen sulphide being at the same time evolved, in consequence of the decomposition of the silver sulphydrate. An excess of silver nitrate must be avoided, as this salt, when boiled for some time with ethyl-sulphocarbimide, converts it into ethyl-cyanate (by substitution of O for S), which is ultimately resolved into carbon dioxide and ethylamine. Most other metallic salts react with ethyl-sulphocarbamic acid in the same manner as silver nitrate. Mercuric chloride is found to be convenient, as it does not attack the ethyl-sulphocarbimide nearly so fast as the silver nitrate; nevertheless a large excess of it should be avoided. In the process just described it is by no means necessary to start with pure ethylamine; the crude mixture of tertiary, primary, and secondary bases and ammonia, obtained by treating alcoholic ammonia with ethyl iodide and distilling with an alkali, answers the purpose quite as well. Diethylamine, in fact, is converted into ethyl-sulphocarbimide quite as easily as ethylamine; it unites with carbon bisulphide, especially in alcoholic solutions, forming diethyl-sulphocarbamate of diethyl-ammonium, which when decomposed with a metallic salt yields a salt of diethyl-sulphocarbamic acid, together with a diethylamine salt, and the former resolves itself into ethyl-sulphocarbimide and a mercaptide:

$$CS\left\{\begin{matrix}N(C^2H^5)^2\\SM\end{matrix}\right. \quad = \quad N\left\{\begin{matrix}CS\\C^2H^5\end{matrix}\right. \quad + \quad S\left\{\begin{matrix}C^2H^5\\M\end{matrix}\right. .$$

Methyl- and amyl-sulphocarbimide may be prepared in a similar manner.

Ethyl-sulphocarbimide, when purified by rectification, is a colourless liquid having a pungent and tear-exciting odour, and producing a burning pain when placed on the skin. It boils at 134°, has a vapour-density of 3·03 (cal. 3·02), and in the liquid state nearly the same specific gravity as water (Hofmann). According to Buff (*Zeitschr. f. Chem.* [2] iv. 730) it boils at 133·2°, and has a sp. gr. of 1·01913–1·019375 at 0°; 0·997525 at 21·4°; 0·997235 at 22°; 0·87909–0·873513 at 133·2°. Ethyl-sulphocyanate, according to the same authority, boils at 146°, and has a specific gravity of 1·03300 at 0°; 1·01261 at 19°; 1·00238 at 23°; 0·870135–0·869367 at 146°.

Ethyl-sulphocarbimide unites directly with *ammonia*, *ethylamine*, *methylamine*, and *aniline*, forming ethyl-, diethyl-, methyl-ethyl-, and ethyl-phenyl-sulphocarbamide (p. 1050).

Ethyl-sulphocarbimide digested for some hours at 110° with *ethyl alcohol*, unites with it, forming ethylic ethyl-oxysulphocarbamate, ethyl-xanthamide, or semi-sulphuretted ethyl-urethane, $CS\left\{\begin{matrix}NH(C^2H^5)\\OC^2H^5\end{matrix}\right.$; and, in like manner, when digested with *mercaptan* at 120°, it forms ethylic ethysulphocarbamate, diethyl-xanthamide, or sulphuretted ethyl-urethane, $CS\left\{\begin{matrix}NH(C^2H^5)\\SC^2H^5\end{matrix}\right.$ (Hofmann, p. 1050).

lxvi. 108) from the greenish-blue decayed wood from which Fordos prepared his xylochloeric acid (v. 1060). To prepare it, the dried and pulverised wood is exhausted with 1 p. c. potash or soda-ley; the filtered and expressed extracts are precipitated with hydrochloric acid; the bulky precipitate is washed with slightly acidulated water, then redissolved in dilute potash-ley, and reprecipitated with alcohol of 85 p. c., and a saturated solution of common salt free from lime and magnesia. Xylindein is thereby precipitated, while humous substances remain in solution. This treatment is several times repeated, and the mass is finally washed with alcohol, dissolved in water, reprecipitated with hydrochloric acid, and dried under the air-pump. Xylindein thus prepared contains 50·33 p. c. carbon, 5·33 hydrogen, 2·63 nitrogen, 41·81 oxygen, and traces of iron and calcium. It is amorphous, and of dark green colour. Water dissolves it easily (in the hydrated state), with splendid green-blue colour; sodium chloride and acids, excepting acetic acid, precipitate it from this solution with green colour. In alkalis and alkaline carbonates, it dissolves very easily with green colour, or greenish-yellow if the alkali is in excess, whereas xylochloeric acid is insoluble in alkalis. Strong sulphuric, nitric, and hydrochloric acid dissolve it, with rapid decomposition. With lime and magnesia it forms lakes insoluble in water, alcohol, &c. It is insoluble in strong alcohol, ether, wood-spirit, carbon bisulphide and benzol; chloroform in contact with hydrated xylindein acquires a faint blue colour. It is reduced like indigo by alcoholic potash and glucose, the solution turning brown. It dyes silk and wool blue-green, without the aid of mordants.

XYLINIC ACID. An acid existing, according, to Lefort (*Compt. rend.* liv. 1235), together with unaltered cellulose, resins, humous substances and salts, in the wood of old oak, elm, and willow stems. It is prepared, like Rommier's xylindein, by extraction with weak alkaline-ley, precipitation with hydrochloric acid, and treatment of the washed precipitate with alcohol and ether. The acid thus obtained is described as a hard, black, tasteless and scentless mass, slightly soluble in water, insoluble in alcohol and ether, easily soluble in alkalis. With the alkalis it forms amorphous brown or reddish salts; its other salts are insoluble. Lefort assigns to the acid the formula $2C^{12}H^{14}O^{8} + H^{2}O$; the barium and calcium salts exhibit corresponding composition.

XYLYL, XYLYLIC ALCOHOL, ACETATE, CHLORIDE, SULPHYDRATE, &c. See the compounds called TOLUYL, TOLUYLIC ALCOHOL, &c., v. 869, 870.

XYLYLAMINES (Pieper, *Ann. Ch. Pharm.* cli. 129).—Bases homologous with the benzylamines, produced by the action of ammonia on xylyl chloride, $C^{8}H^{9}Cl = C^{6}H^{4}\left\{\begin{matrix}CH^{3}\\CH^{2}Cl\end{matrix}\right.$. This chloride, prepared by passing chlorine into xylene at the boiling point, is heated in sealed tubes to 116° with strong alcoholic ammonia; the contents of the tubes are thrown on a filter; and the crystalline mass, containing a large quantity of sal-ammoniac, is washed several times with alcohol. The filtrate freed by distillation from the ammonia and the greater part of the alcohol, is then mixed with water, which throws down impure oily trixylylamine $(C^{8}H^{9})^{3}N$; and the crystalline mass remaining on the filter is drenched with water, which dissolves the hydrochlorides of xylylamine and dixylylamine, leaving trixylylamine undissolved. The solution of the mixed hydrochlorides when concentrated, first deposits the dixylylamine salt, which may be purified by recrystallisation; the mother-liquor, evaporated to a small bulk and mixed with strong potash-ley, yields an oil consisting of xylylamine salt mixed with dixylylamine; and on drying this oil over sticks of potash and distilling at 210°, xylylamine passes over, while the dixylylamine remains behind.

Xylylamine, $C^{8}H^{11}N = N\left\{\begin{matrix}C^{8}H^{9}\\H^{2}\end{matrix}\right.$, isomeric with xylidine, is a colourless, oily, strongly alkaline liquid, smelling like herring-pickle, floating on water, and boiling at 196°. It is soluble in alcohol and ether, insoluble in water. When exposed to the air, it rapidly absorbs carbonic acid and becomes solid. Its solution in dilute alcohol precipitates the hydrates from many metallic salts. The *hydrochloride*, $C^{8}H^{11}N.HCl$, crystallises in white needles, easily soluble in water and alcohol, and melting at 185°. The *platinochloride*, $2(C^{8}H^{11}N.HCl).PtCl^{4}$, forms golden-yellow shining laminæ. With *mercuric chloride* also xylylamine hydrochloride forms a double salt which separates in white crystals.

The isomerism between xylylamine and xylidine or amidoxylene is represented by the following formulæ:

Allyl-sulphocarbimide, or *Volatile oil of Mustard*, $N\left\{\begin{matrix}CS\\C^3H^5\end{matrix}\right.$ — It is remarkable that this compound, which exhibits all the essential characters of the sulphocarbimides above described, has not hitherto been produced artificially by analogous processes, but is obtained by a reaction which might rather be expected to yield allyl sulphocyanate, $S\left\{\begin{matrix}CN\\C^3H^5\end{matrix}\right.$, viz. by distilling potassium sulphocyanate with allyl iodide (v. 516), or with allyl bromide, or with the potassium salt of allyl-sulphuric acid. The product obtained by either of these processes is identical in every respect with natural oil of mustard (Tollens, *Zeitschr. f. Chem.* [2] v. 90).

Mustard-oil heated with *alcohol* a little above 100° unites with it, forming semi-sulphuretted allyl-urethane, $CS\left\{\begin{matrix}NH(C^3H^5)\\OC^2H^5\end{matrix}\right.$ (Hofmann, p. 1050). According to L. Henry (*Jahresb.* 1867, p. 379), it unites directly with dry *hydrobromic acid*, forming a crystalline compound, from which it is separated by water. With dry *hydriodic acid* it forms a pitchy mass. Heated in alcoholic solution with *zinc* and *hydrochloric acid*, it is converted into allylamine, hydrogen sulphide, and carbon dioxide:

$$N\left\{\begin{matrix}CS\\C^3H^5\end{matrix}\right. + 2H^2O = N\left\{\begin{matrix}C^3H^5\\H^2\end{matrix}\right. + H^2S + CO^2$$

(Oeser, *Ann. Ch. Pharm.* cxxxiv. 7).

The following normal sulphocyanic ethers have been prepared by L. Henry (*Deut. chem. Ges. Ber.* ii. 207; *Zeitschr. f. Chem.* [2] v. 206).

Benzyl Sulphocyanate, $C^7H^7.CNS$ or $S\left\{\begin{matrix}CN\\C^7H^7\end{matrix}\right.$, is produced by heating benzyl-chloride with potassium cyanate in a water-bath, and crystallises from alcohol in large transparent prisms, insoluble in water, slightly soluble in cold alcohol, easily in hot alcohol, also in ether and in carbon bisulphide. It has a sharp smell and taste, melts at 36°–38°, and boils with partial decomposition at 256°. It unites readily with dry gaseous hydrogen bromide, forming a crystallised compound, insoluble in ether, immediately decomposed by water. Fuming nitric acid converts it into *nitro-benzyl sulphocyanate*, $C^7H^6(NO^2).CNS$, which is also produced from nitrobenzyl chloride, $C^7H^6(NO^2)Cl$, and potassium sulphocyanate, and crystallises from alcoholic solution in small brittle needles, volatilising at about 70°, and decomposing before it distils.

Glyceryl Sulphocyanate, $C^3H^5(CNS)^3$, is prepared by the action of potassium sulphocyanate in alcoholic solution at 100° on isotribromhydrin (produced by the action of bromine on allyl iodide); ordinary trichlorhydrin does not yield it. The compound separates from the alcoholic liquid in the crystalline form, and when recrystallised from alcohol forms small, white, shining, hard, brittle needles, having neither taste nor smell. It melts at 126°, and soon afterwards decomposes, giving off hydrogen cyanide and leaving a carbonaceous residue. It is quite insoluble in water, very slightly soluble in cold alcohol, much more soluble in boiling alcohol (Henry).

General Reactions of the Sulphocarbimides and Sulphocyanic Ethers.—The bodies of both these groups (taking the methyl-compounds for example) are ultimately produced from methyl-alcohol, carbon bisulphide, and ammonia, with elimination of 1 mol. water and 1 mol. hydrogen sulphide:

$$CH^4O + CS^2 + NH^3 = H^2O + H^2S + C^2H^3NS,$$

the nature of the resulting compound depending only on the order in which the reactions take place. In the case of methyl-sulphocarbimide we have:

$$(1)\ .\ .\ CH^4O + NH^3 = H^2O + N\left\{\begin{matrix}CH^3\\H^2\end{matrix}\right.$$

$$(2)\ .\ .\ N\left\{\begin{matrix}CH^3\\H^2\end{matrix}\right. + CS^2 = H^2S + N\left\{\begin{matrix}CS\\CH^3\end{matrix}\right.$$

and in that of methyl-sulphocyanate (see v. 504):

$$(1)\ .\ .\ NH^3 + CS^2 = H^2S + S\left\{\begin{matrix}CN\\H\end{matrix}\right.$$

$$(2)\ .\ .\ S\left\{\begin{matrix}CN\\H\end{matrix}\right. + CH^4O = H^2O + S\left\{\begin{matrix}CN\\CH^3\end{matrix}\right.$$

These considerations are supported by the following reactions: When an alcoholic solution of ethyl-sulphocarbimide is mixed with *zinc* and *hydrochloric acid*, hydrogen sulphide is given off for several days in continually decreasing quantity, but no carbon dioxide, whilst the liquid becomes filled with white needles of formic sulphaldehyde, Pure zinc with metallic surface is scarcely attacked by dilute sulphuric acid $SO^3.9H^2O$; much more easily after its surface has become covered by exposure with a thin film of oxide. The action of the strong acid ($SO^3.H^2O$ and $SO^3.2H^2O$) takes place at high temperatures, with evolution of sulphurous oxide; that of the weaker acid ($SO^3.3H^2O$ to $SO^3.6H^2O$) with continuous evolution of hydrogen sulphide and a small quantity of sulphurous oxide; and that of still weaker acid, with evolution of pure hydrogen.

In a solution of *sodium chloride* zinc dissolves with evolution of hydrogen, formation of zinc-sodium chloride, and separation of zinc oxide. The oxide dissolves in solution of sodium chloride, slowly in the cold, more quickly and abundantly when heated, the liquid acquiring an alkaline reaction (Siersch, *Jahresb.* 1867, p. 257).

On the volumetric estimation of zinc by means of potassium ferrocyanide, see Renard (*Compt. rend.* lxvii. 450; *Jahresb.* 1868, p. 874; *Bull. Soc. Chim.* [2] xi. 473; *Zeitschr. f. Chem.* [2] v. 662).

For the separation of zinc from copper (in brass), Chancel mixes the solution of the two metals with *sodium thiosulphate* till it is completely decolorised. Sodium carbonate then precipitates the zinc, while the copper remains in solution. A small quantity of copper still remaining in the zinc carbonate may be removed by precipitation with hydrogen sulphide in acid solution (*Jahresb.* 1866, p. 803).

According to Schweikert (*Jahresb.* 1867, p. 847) zinc cannot be completely separated from phosphoric acid by fusion with sodium carbonate and lixiviation of the fused mass with water, inasmuch as part of the phosphoric acid remains combined with zinc oxide, and part of the latter passes into solution as sodium zincate. Moreover zinc oxide is not quite insoluble in sodium carbonate, and is not precipitated from the solution even by prolonged boiling. In precipitating zinc as carbonate, it is therefore necessary to avoid a large excess of sodium carbonate, or to neutralise it before heating.

An alloy of zinc and calcium containing 95·13 p. c. zinc, and 4·87 calcium, or $Zn^{12}Ca$, crystallises in obtuse quadratic octohedrons having a sp. gr. of 6·369 to 6·3726 (determined under rock-oil); it is decomposed by water (G. vom Rath, *Zeitschr. f. Chem.* [2] v. 665).

Commercial zinc-dust from the Rostberg works, was found by Aldendorf (*Jahresb.* 1866, p. 219) to consist of

Zn	Pb	Cd	ZnO	$ZnCO^3$	Insoluble matter
39·99	2·47	4·09	49·76	3·29	0·39

In consequence of the fine division of the zinc, this dust slowly decomposes water at ordinary temperatures, eliminating in 24 hours about its own volume of hydrogen. On leaving it in contact with dilute hydrochloric or sulphuric acid till hydrogen begins to escape, the greater part of the zinc oxide and carbonate are dissolved, while the metal remains as a fine grey powder, which when washed is well adapted for a reducing agent.

A compound of *zinc chloride* with *ammonia*, $ZnCl^2.5NH^3 + H^2O$, is formed when solid zinc chloride is gradually added to strong well-cooled aqueous ammonia, gaseous ammonia being passed into the liquid towards the end of the process. As soon as a considerable precipitate has formed, the vessel is to be closed, gently warmed till the whole is dissolved, and left to cool. The ammonio-chloride then separates in regular octohedrons, with step-like cavities in their faces. The crystals when exposed to the air, immediately give off ammonia, become moist, and ultimately appear corroded and deliquesced. They dissolve easily in water, still more easily, with decomposition, in aqueous zinc chloride (E. Divers, *Chem. News*, xviii. 13); compare v. 1069.

Zinc Phosphides.—B. Renault (*Ann. Ch. Phys.* [4] ix. 162), by heating to whiteness a mixture of 1 mol. magnesium phosphate, ($Mg^2H^2P^2O^8$), 2 mol. zinc sulphide, and 7 at. carbon, in a coated retort connected with a red-hot earthen receiver, has obtained the following compounds of zinc and phosphorus: 1. A massive phosphide Zn^3P^2 of leaden colour and sp. gr. 1·21 at 14°. It is moderately permanent in the air, less fusible than zinc, and volatilises slightly above its melting point; heated with lead sulphide, it is converted into zinc sulphide, with separation of lead and phosphorus; it is also converted into sulphide by digestion with carbon bisulphide.—2. The same compound is obtained crystallised in interlaced needles having a faint metallic lustre, when the vapours are condensed in a larger and more strongly heated receiver. This crystallised phosphide is more easily alterable than the compact variety; gives off hydrogen phosphide in contact with the air; and is violently attacked by acids.—3. In certain preparations the needles were mixed with more brilliant and permanent crystals having the composition Zn^2P^2.—4. In capacious receivers there were also formed orange-coloured to cinnabar-red or metallically lustrous interlaced needles, which, when heated in the air, burned with a phosphorus flame, leaving zinc phosphate. The red compound was likewise obtained, together with metallically lustrous needles, when phosphorus vapour, mixed with not perfectly dry hydrogen, was passed over red-hot zinc, or phosphorus vapour over red-hot zinc oxide: it appears to be an oxyphosphide varying in composition from ZnP^2O to $Zn^3P^{10}O^4$; the metallically lustrous needles exhibited the composition $Zn^7P^{14}O^4$. The red compound is dissolved by hot hydrochloric and sulphuric acids, with formation of phosphorous acid.—5. A red phosphide, Zn^3P^4, was obtained by treating a mixture of the crystalline oxyphosphides with hydrochloric acid.—6. On dissolving a large quantity of the compound Zn^3P^2 in dilute hydrochloric, sulphuric, or nitric acid, another phosphide, ZnP^6, remained behind, as a yellow, amorphous, very inflammable powder, which detonated with the greatest violence, both when brought in contact with nitric acid and when mixed with potassium chlorate and lightly struck. The composition of all these zinc phosphides must be regarded as doubtful.

ZINC-ETHYL and **ZINC-METHYL.** $Zn(C^2H^5)^2$. For the preparation of zinc-ethyl, Wichelhaus heats zinc filings with iodide or bromide of ethyl in the water-bath in a retort with upright condenser, the pressure being increased by a column of mercury. The reaction is said to be finished in two or three hours, and to yield from 80 to 90 p. c. of the theoretical quantity (*Jahresb.* 1868, p. 428).

A mixture of zinc-ethyl with about twice its volume of *carbon bisulphide*, in a tube filled with carbon dioxide, begins to boil spontaneously, passing through all shades of red-brown till it becomes quite opaque, giving off at the same time a combustible gas consisting of hydrogen sulphide, vapour of carbon bisulphide, and ethylene. On the completion of the reaction, first at 50°–60°, afterwards at 100° in a sealed tube, the contents of the tube, freed from excess of carbon bisulphide, consist of a brown shining mass, which, according to its weight and composition (somewhat variable indeed in different preparations), appears to consist of $C^5H^{10}S^2Zn = CS^2 + Zn(C^2H^5)^2$. This compound is insoluble in water, alcohol, and ether, but dissolves in acids with evolution of hydrogen sulphide. When subjected to dry distillation, or heated with hydrochloric acid, it gives off an oil having a pungent alliaceous odour, and boiling between 80° and 180°, the principal portion, which passes over between 130° and 150°, having the composition of amylene sulphide, $C^5H^{10}S$. When the purified oil is mixed in warm alcoholic solution with mercuric chloride, a white flocculent precipitate is formed, and the quickly filtered liquid deposits when heated iridescent laminæ having the composition $C^5H^{10}S.HgCl^2.HgS$. The amorphous substance separated by filtration appears to have the same composition as the crystals. With silver nitrate, in like manner, yellow microscopic needles are obtained, having the composition $C^5H^{10}O.Ag^2O.AgNO^3$. From the composition of the principal product, $C^5H^{10}S = CS(C^2H^5)^2$, it may be inferred that the action of zinc ethyl on carbon bisulphide takes place according to the equation:

$$CS^2 + Zn(C^2H^5)^2 = C^5H^{10}S.ZnS.$$

Zinc-methyl unites with carbon bisulphide in a similar manner. Zinc-ethyl and *mustard oil* likewise form a brown amorphous zinc-compound difficult to isolate (Grabowski, *Ann. Ch. Pharm.* cxxxviii. 165).

According to Butlerow (*ibid.* cxliv. 39) the vapours of zinc-methyl, though they have a disagreeable odour and excite coughing, are not poisonous.

ZIRCON. Certain zircons, of the variety called jargon, exhibit, both in their natural state and when fused with borax, very remarkable spectra, which were first described by Sorby (*Proc. Roy. Soc.* xvii. 511; *Chem. News*, xix. 122), and were supposed to indicate the presence of a new element, which was called *Jargonium*. Methods of obtaining jargonia, the oxide of this metal, and separating it from zirconia, and descriptions of its properties, were given by Sorby (*loc. cit.*) also by Church (*Chem. News*, xix. 121, and Loew, *ibid.* xx. 9). More recently, however, Sorby has shown that the peculiar spectra in question are due to the presence of certain compounds of uranic oxide with zirconia, these compounds giving spectra containing dark bands not exhibited either by uranic oxide or by zirconia alone. Artificially prepared compounds of uranic oxide with pure zirconia exhibit exactly the same spectra as those of the natural mineral. Hence Sorby concludes that the supposed jargonium has no existence (*Chem. News*, xxi. 73).

R. Hermann (*J. pr. Chem.* xcvii. 321; *Jahresb.* 1866, p. 191) has confirmed the results obtained by Berlin, respecting the earth called noria, found by Svanberg in the zircons of Norway and other localities. Hermann's experiments show that zirconia, when contaminated with small quantities of alumina, exhibits properties exactly like those of the supposed noria.

Zirconia has lately been brought into use in the oxyhydrogen blowpipe in place of lime or magnesia. It possesses great radiating power and is very refractory, remaining quite unaltered after a month's use. To economise the costly material, only the outer portion of the cylinder is made of zirconia, the interior being composed of magnesia or fire-clay, the two substances being firmly pressed together. (See *Compt. rend.* lxvi. 1040: *Ann. Ch. Phys.* [4] xiv. 11; *Dingl. pol. J.* clxxxix. 116: cxci. 252; *Zeitschr. f. Chem.* 1868, p. 536; *Chem. News*, xviii. 276).

ADDENDA.

INDIUM. According to a recent determination by Bunsen (*Pogg. Ann.* cxli. 1; *Chem. Soc. J.* [2] ix. 182), the specific heat of this metal is 0·57. This number multiplied by 75·63, the hitherto received atomic weight of indium (p. 729), gives for the atomic heat, the number 4·3, which does not agree with the law of Dulong and Petit. But if the atomic weight be taken as 1½ times 75·6, or 113·4, the atomic heat becomes 6·5, which agrees nearly with the general law.

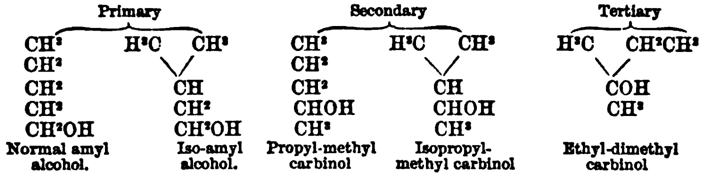
On this view, indium must be regarded as triatomic, and the formulæ of its principal compounds will be as follows:

Chloride	$InCl^3$
Indium and ammonium chloride . .	$2NH^4Cl.InCl^3 + H^2O$
Yellow oxide	In^2O^3
Normal hydrate	InH^3O^3
Nitrate	$In(NO^3)^3$
Sulphate	$In^2(SO^4)^3 + 9H^2O$
Black oxide	InO^2
Green oxide	$2InO.In^2O^3$
Grey oxide	$3InO.2In^2O^3$

NORMAL AMYL-COMPOUNDS. The specific gravities and boiling points of some of these compounds, as determined by Lieben a. Rossi (*Gazzetta chimica italiana*, i. 314), are as follows:

	Boiling point		Specific gravity at 0°	20°	40°
Alcohol . .	137°	(bar. at 0·740 met.)	0·8296	0·8168	0·8065
Chloride .	106°	„ 0·7398 „	0·9013	0·8834	0·868
Bromide .	128·7°	„ 0·7394 „	1·246	1·2234	1·2044
Iodide . .	155·4°	„ 0·7393 „	1·5435	1·5174	1·4961
Acetate . .	148·4°	„ 0·737 „	0·8963	0·8792	0·8645

The boiling points of the five known amyl alcohols go on increasing from the tertiary to the normal primary, as will be seen from the following comparison:



Normal amyl alcohol.	Iso-amyl alcohol.	Propyl-methyl carbinol	Isopropyl-methyl carbinol	Ethyl-dimethyl carbinol
B. P. 137°	128°–132°	120°–123°	104°–108°	98·5°–100°

NORMAL CAPROIC ACID, $CH^3CH^2CH^2CH^2CH^2.COOH$, is prepared by heating normal amyl bromide or iodide to 105° in a sealed tube with pulverised potassium cyanide dissolved in alcohol of 85° p. c., and heating the resulting normal amyl cyanide with alcoholic potash in an apparatus with reversed condenser. On distilling the resulting potassium salt with dilute sulphuric acid, and purifying the oily layer which separates by washing and distillation, normal caproic acid is obtained as a colourless liquid, which does not mix with water, has an odour fainter and somewhat less disagreeable than that of ordinary caproic acid, and a strongly acid taste. It boils at 204·5° (bar. at 0·7385 met.); the caproic acid prepared from ordinary amyl cyanide boils at 198° (Wurtz), at 199·7 (Lieben a. Rossi). The normal acid has a specific gravity of 0·9449 at 0°, 0·9294 at 20°, 0·9172 at 40°, and 0·8947 at 99·1° (Lieben a. Rossi, *loc. cit.*).

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OXYGEN-COMPOUNDS OF SULPHUR.

1. **Hyposulphurous Acid.** $H^2SO^2 = \left.\begin{matrix}H\\H\end{matrix}\right\}SO^2$.—*Hydrosulphurous Acid* (Schützenberger, *Zeitschr. f. Chem.* [2] v. 545).—This acid is produced by the action of zinc on aqueous sulphurous acid. The metal dissolves without evolution of hydrogen, forming a yellow solution which possesses a decolorising power much greater than that of sulphurous acid itself, throws down from cupric sulphate a precipitate of copper hydride, Cu^2H^2, mixed, if the copper solution is in excess, with metallic copper, and immediately reduces the metals from silver and mercury salts. The solution thus obtained is, however, very unstable; its decolorising power attains a maximum in a few minutes, then diminishes, while at the same time it loses its yellow colour and becomes milky from separation of sulphur; it then contains thiosulphuric acid, $H^2S^2O^3$.

A more definite product is obtained by immersing clippings of zinc in a concentrated solution of acid sodium sulphite contained in a closed vessel. The zinc then dissolves as before without evolution of hydrogen, the reaction being completed in about half an hour, and an abundant crystallisation of zinc-sodium sulphite is produced. The decanted liquid, which possesses very great decolorising power, becomes very hot on exposure to the air, losing at the same time its characteristic properties, and afterwards containing nothing but the double salt just mentioned, together with acid sodium sulphite. To isolate a definite compound, the solution (about half a litre) is poured into a flask holding about two litres, and three-fourths filled with strong alcohol, and the flask is hermetically sealed. A crystalline precipitate is then immediately formed, consisting for the most part of zinc-sodium sulphite, while nearly all the bleaching compound remains dissolved in the alcohol. This solution decanted into a flask quite filled with it, well closed, and left to stand in a cool place, solidifies in a few hours to a mass of slender colourless needles, which must be pressed as quickly as possible between folds of linen, and dried in a vacuum, as it becomes very hot if exposed to the air in the moist state; when dry, however, it is not affected by oxygen. This salt contains but a small quantity of zinc, from which it may be freed by solution in water and reprecipitation with alcohol. It then consists of *sodium hyposulphite*, $NaHSO^2$. It is very soluble in water, soluble also in dilute alcohol, insoluble in strong alcohol. Its solution possesses all the decolorising and reducing powers above mentioned. The crystals when exposed to the air are completely converted into acid sodium sulphite, $NaHSO^3$, without formation of other products. When heated in a tube, they give off sulphur and sulphurous acid, together with a little water, and leave a residue of sodium sulphate and sulphide.

Hyposulphurous acid, which is much more unstable than its sodium salt, may be separated therefrom by treating the crystals with oxalic acid. A deep orange-yellow solution is then formed, possessing great decolorising power, and quickly becoming colourless, with deposition of sulphur. The formation of the acid by the action of zinc on sulphurous acid is represented by the equation:

$$H^2SO^3 + Zn = ZnO + H^2SO^2.$$

The same reaction takes place with other metals, as iron or manganese. The formation of thiosulphates in all these cases is only a secondary reaction due to the slow and spontaneous decomposition of the hyposulphite.

When a porous earthenware cell filled with acid sodium sulphite is immersed in weak sulphuric acid, and the liquid subjected to electrolysis, the negative pole dipping into the acid sulphite, oxygen is evolved at the positive pole, while at the negative pole no gas is evolved, but the sulphite is converted into hyposulphite. By replacing the nitric acid in a Bunsen's cell with acid sodium sulphite, a combination is obtained, which is very little inferior in intensity to the ordinary Bunsen's battery, and remains constant for a considerable time (Schützenberger).

Ethyl-hyposulphurous Acid. $C^2H^6SO^2 = \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}SO^2$ (Wischin, *Ann. Ch. Pharm.* cxxxix. 364).—This acid, called by its discoverer *ethyl-sulphurous acid*, is produced as a zinc-salt by the action of zinc-ethyl on sulphuric anhydride, $2SO^3 + Zn(C^2H^5)^2 = SO^2 + ZnSO^4 + C^4H^{10}$; and $2SO^2 + Zn(C^2H^5)^2 = Zn(C^2H^5SO^2)^2$. When zinc-ethyl is carefully mixed with an equivalent quantity of sulphuric anhydride in a strong tube sealed and filled with dry carbon dioxide, a violent reaction takes place, very apt to give rise to explosion, and zinc ethyl-hyposulphite is formed, together with combustible gases, sulphurous anhydride, zinc sulphate, zinc sulphide, and metallic zinc. Ethyl-hyposulphurous acid is also formed (contrary to the

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